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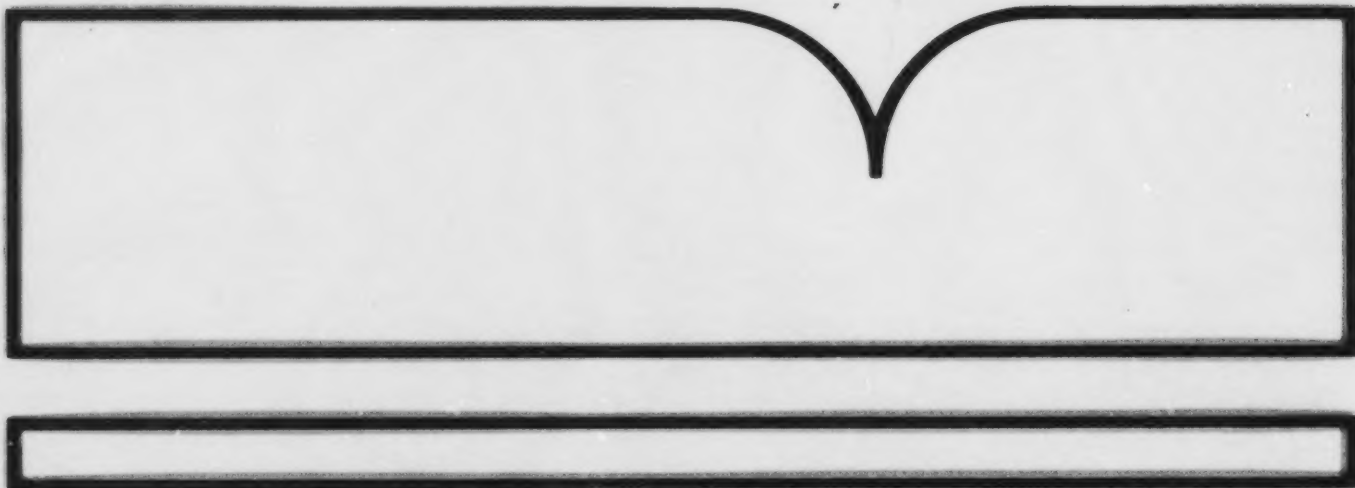
Findings of the Chlorofluorocarbon
Chemical Substitutes International Committee

Radian Corp., Austin, TX

Prepared for

Environmental Protection Agency
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FINDINGS OF THE CHLOROFLUOROCARBON
CHEMICAL SUBSTITUTES INTERNATIONAL
COMMITTEE

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EPA Contract No. 68-02-3994
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FOREWORD

Faced with mounting scientific evidence that the Earth's protective shield of stratospheric ozone could be threatened by certain long-lived, potentially ozone-depleting chemicals released into the atmosphere from anthropogenic sources, the U.S. Environmental Protection Agency announced in January, 1986, a plan to protect the ozone layer. This plan contained three primary elements: (1) conducting research and analyses in several subject areas related to the issue in order to narrow scientific and economic uncertainties, (2) conducting and participating in conferences and workshops both in the U.S. and abroad aimed at arriving at a better understanding of all aspects of the issue, and (3) deciding upon the need for and means of implementing additional domestic regulation of fully-halogenated chlorofluorocarbons (CFCs) in concert with similar actions worldwide.

Early in EPA's analyses, it became apparent that the substitution of suspect CFCs with more environmentally benign chemicals was at least one possible remedy worthy of consideration. However, it was also apparent that few, if any, alternative chemicals were readily available or had been proven to be suitable for the multitude of CFC uses. Accordingly, EPA sought to improve its understanding of possible CFC chemical alternatives by convening a committee of experts in the field of CFC synthesis and industrial production. Dr. Richard Lagow was such a recognized expert and accepted the challenge of assembling and chairing such a committee.

This report presents the results of the Committee's deliberations on such matters as the necessary steps remaining to commercialize leading candidate substitutes, identification of several secondary candidates, and additional research needed to resolve uncertainties.

The EPA expresses its gratitude for the excellent efforts of Dr. Lagow and all Committee members, and believes the information reported here to be a valuable contribution in developing safeguards against the human health and environmental risks that would occur from depletion of stratospheric ozone.

John S. Hoffman, Director
EPA Stratospheric Ozone Protection
Program

ABSTRACT

This report presents the findings of a select international committee of experts from industry and academia on the subject of chemical substitutes for fully-halogenated chlorofluorocarbons (CFCs). This committee, over the course of two meetings, reviewed and discussed data and information on chemical alternatives for fully-halogenated CFCs now in use. Also, committee members prepared brief reports highlighting specific areas of concern.

FC-134a was identified as having the greatest current potential for replacing CFC-12, and similarly CFC-123 could replace CFC-11. The committee acknowledged that while there are numerous other possible chemical replacements, there is a dearth of information on these compounds with regard to property data, toxicity, and performance in end-use applications.

Investigation of new chemicals to serve as "back-up" candidate substitutes in the event that FC-134a and CFC-123 fall short of expectations was strongly recommended. Such investigations should include a preliminary screening of chemical, physical, and thermodynamic properties; acute toxicity; and likely atmospheric fate. Finally, several new chemicals were suggested for examination.

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SECTION 1

INTRODUCTION

BACKGROUND

A family of chemicals known as chlorofluorocarbons (CFCs) has been implicated in the depletion of the earth's stratospheric ozone layer. A number of adverse health and ecological effects could result from such depletion. For this reason a number of strategies or options for controlling the atmospheric release of these compounds are being evaluated by governments and industries worldwide. One promising approach appears to be the substitution of new, low ozone-depleting CFCs for those currently employed in a wide variety of end uses. There is a need, however, to better define the requirements for developing and bringing to market these new substitutes. To this end, a committee of the foremost authorities in CFC chemistry, production, toxicology, and marketing was assembled to ascertain the degree of promise of this approach and what steps must be taken by industry and government to achieve such substitution in the most efficient and timely manner.

Committee members were assembled by Richard Lagow of the Chemistry Department, University of Texas at Austin. Committee members were selected on the basis of their internationally recognized expertise in chlorofluorocarbon chemistry, properties, and production and included chemists, engineers, toxicologists, and members of industry. Table 1-1 presents the list of committee members and their affiliations.

PROJECT OBJECTIVES

The overall objective of the Committee was to comment on the commercialization potential of newer CFC chemical substitutes for the

TABLE 1-1. CFC CHEMICAL SUBSTITUTES INTERNATIONAL COMMITTEE

R.E. Banks	University of Manchester (UK)
Joseph F. Borzelleca	Medical College of Virginia
Luther C. Chien	E.I. DuPont deNemours & Company
Darryl D. DesMarteau	Clemson University
Nobuo Ishikawa	F&F Research Center (Japan)
Richard Lagow, Chair	University of Texas at Austin
J. Donald LaZerte	3M Company (retired)
John L. Margrave	Rice University
Martin A. Robinson	Allied-Signal, Inc.
Herbert W. Roesky	Universitat Gottingen (Fed. Rep. of Germany)
Eugene Stump	Consultant
Andrew J. Woytek	Air Products and Chemicals, Inc.
Masaaki Yamabe	Asahi Glass Co., Ltd. (Japan)

suspect ozone depleting chemicals: CFC-11 (trichlorofluoromethane), CFC-12 (dichlorodifluoromethane), and CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane).

Specific objectives included:

- Identify the most promising newer CFC chemical substitutes;
- Estimate cost, quantities of chemicals required, and time for toxicity testing, application testing, and commercialization of these substitutes;
- Specify necessary market and price preconditions for commercialization;
- Recommend research and development tasks to assist commercialization; and
- Suggest possible communications between CFC producers and potential users regarding research activities.

These objectives were to be addressed by developing consensus opinions of the committee members.

APPROACH

The CFC Chemical Substitutes International Committee met on two different occasions. The first was February 19 through 21, 1987 in Washington, D.C. A second meeting was held in Yountville, California on April 22 through 24, 1987. At the first meeting, committee members became more familiar with the CFC environmental issues through direct discussions with U.S. EPA officials. Also, the committee formulated their initial thoughts on additional CFC chemical substitutes, costs, toxicology, and commercialization potentials.

The second workshop was primarily for the purpose of completing the definition of the issues and organizing an approach to addressing the issues. Based on results of the first meeting, the second meeting also included interactions with CFC users from industry. CFC users represented were automobile air conditioning (Norman Nielson of Chrysler Motors), refrigeration and air conditioning (Wayne Reedy of Carrier Corporation), and foam insulation board (Joseph Hagan and John Oliver of Jim Walter Research Corporation). In addition, F. Sherwood Rowland (University of California-Irvine), one of the originators of the ozone depletion theory, gave a presentation on atmospheric chemistry that focused on current knowledge of stratospheric chemistry and ozone depletion potential of newer CFC chemical substitutes.

Deliberations of the committee were summarized as a formal press release and as a joint EPA-Committee Statement. These statements are presented in Section 3 of this report. Also, individual panel members drafted brief reports on specific aspects of the issues. These reports are presented in Appendices A through K. An executive summary for the project was prepared by Richard Lagow, committee chairman, and is given in Section 2. Section 4 presents an approach for categorizing possible chemical alternatives for fully-halogenated CFCs.

SECTION 2

EXECUTIVE SUMMARY

Richard Lagow, Chairman

In view of the mounting global concern over depletion of ozone in the stratosphere and the probability that certain commercial chlorofluorocarbon products may play a significant role in such depletion, an international scientific committee was assembled. The mandate of this committee was to identify the most promising chemical substitutes for CFC-11, CFC-12, and CFC-113, and to establish and consider all factors which influence commercialization of these substitutes. The committee was asked particularly to make recommendations to facilitate availability of chemical substitutes, and to identify and analyze factors which could accelerate the timescale for availability of such substitutes.

The most important findings of this panel were that FC-134a was the primary replacement candidate for CFC-12 and CFC-123 was determined to be the primary replacement candidate for CFC-11. The Committee advocated incentives for increasing the use of CFC-22 in refrigeration markets and other applications. Also recommended was a strong conservation and recycling program for CFC-113 which is of key importance as a solvent in cleaning applications in the electronics industry and for metal cleaning applications. The Committee identified many other potential substitutes and recommended further research on these materials.

The international panel was funded by the U.S. Environmental Protection Agency and organized through the EPA Office of Air and Radiation under John S. Hoffman, Director, Strategic Studies Staff, who developed the concept for such a committee. The coordinators for the EPA were Neil Patel and N. Dean Smith; Radian Corporation of Austin, Texas served as the General Contractor. The international panel was chaired by Richard Lagow of the University of Texas at

Austin. The panel was composed of three prominent U.S. academic fluorocarbon chemists (Darryl DesMarteau, John Margrave, and Richard Lagow) along with distinguished academic fluorocarbon chemists from each of several countries (R.E. Banks, Britain; Herbert W. Roesky, West Germany; Nobuo Ishikawa, Japan) and an outstanding toxicologist, Joseph Borzelleca of the Medical College of Virginia. The panel also included distinguished industrial chemists and managers such as J. Donald LaZerte, former Technical Director of the Industrial Chemical Products Division of 3M Company; Luther C. Chien, former Director of Research of the DuPont Freon Division; Martin A. Robinson, Director of the Fluorine Research Laboratory for Allied-Signal; Eugene Stump, formerly Vice President of PCR, Inc.; Andrew J. Woytek, Director of Research of the Specialty Gases Division of Air Products and Chemicals, Inc.; and Masaaki Yamabe, Director of Chemical Research, Asahi Glass Co., Ltd., one of Japan's most innovative fluorochemical organizations.

Of the many barriers and potential barriers to availability of appropriate quantities of alternative chlorofluorocarbon and fluorocarbon compounds, the Committee concluded that the most basic was the lack of a market worldwide for such materials. Such a market can only be created by government regulations worldwide to create a demand for such materials. It should be noted that the chemical manufacturing process (Swarts reaction and improved versions) producing the currently marketed chlorofluorocarbons delivers these products at such a low price (1.30 to 1.75 dollars per kilogram) that the performance-cost ratio for a variety of applications is among the highest known for commercial chemicals. This accounts for their extraordinarily large market and widespread use even in applications for which they are not unique. The essentially nonflammable and nontoxic characteristics at 1.30 to 1.75 dollars per kilogram, which are primary reasons for use in many applications, cannot be duplicated at that price. This price follows from the fact that very inexpensive hydrogen fluoride and chlorocarbons (from petrochemical feedstock and inexpensive chlorine gas derived through chloro-alkali chemistry of sodium chloride) are primary feedstocks. The Committee noted that there would be a very small market or no market for performance effective new

materials at even a price as low as \$2.00 per pound (\$4.40 per kg). The Committee recommends that governments around the world institute regulations which would make such new chlorofluorocarbon alternative chemicals economically viable and establish a market with suitable incentive for the chemical industry worldwide to enter the market with new compounds which have markedly lower ozone depletion potential and greenhouse gas effects. While there has been some criticism directed toward U.S. chemical companies along the lines that it would be unlikely that they would develop and market such alternatives without regulatory incentives, in fact, it is very unlikely that users will, without regulation, be unilaterally willing to pay higher prices for they are in competitive situations and may not be able to sacrifice to become "better world citizens." The Committee identified the factors that influence the commercialization timescale for new compounds as well as the already known substitutes such as FC-134a, CFC-123, etc. The Committee studied exhaustively factors which influence this timescale. The Committee looked objectively at an optimal timescale presented by Luther Chien of DuPont (Figure 1) and came to a consensus that this chart represents a fair analysis. Probably the best overview is that commercial quantities of such new materials could be available in a minimum of five years and a maximum of ten years (Appendix F).

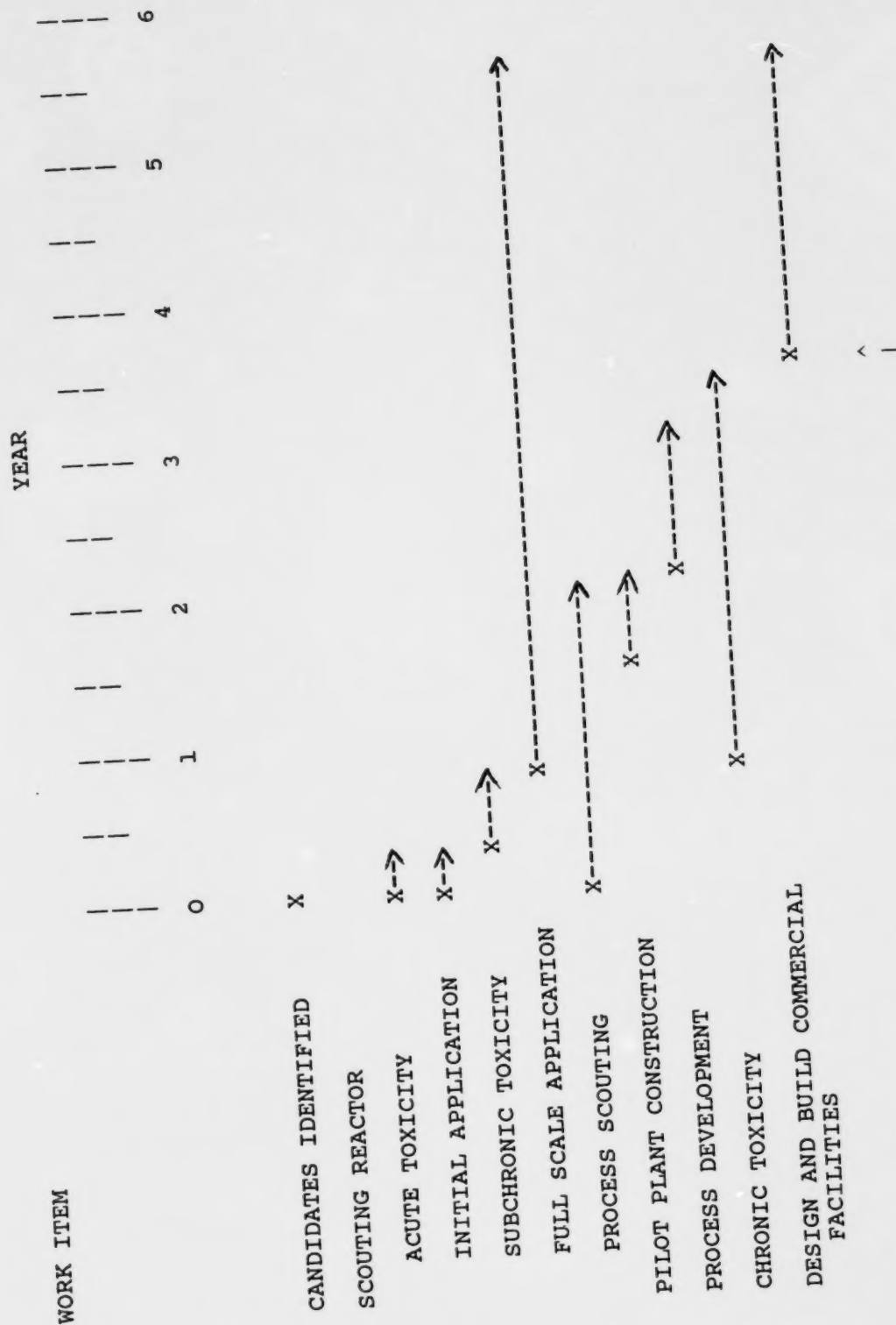
Analyzing each component of the timing, the Committee found that even in view of the substantial effort required for research and development and effort to design and build commercial facilities, or alter existing commercial facilities, the most time intensive part of the process of bringing a new material to the market to be the chronic inhalation toxicity testing. (For a detailed discussion of the 3-tier toxicological testing, please refer to Joseph Borzelleca's report in Appendix B). This phase requires up to four years and proceeds in the normal industrial environment after initial market analysis for the compound appears favorable and after acute and subchronic testing comes to a favorable conclusion. In view of the time criticality associated with chronic inhalation studies and reproductive toxicity studies, some members of the Committee favored immediate U.S. government funding of

tier 3 (chronic) toxicity testing of "pure" samples of obvious substitute candidates such as FC-134a and CFC-123 noting that the \$3 million cost was very acceptable if it could cut six months to a year off the timescale for commercialization. It was further noted that such an early investment could be very advantageous in starting other new materials down the path sooner in the event of tier 3 toxicity failure of such materials as FC-134a and CFC-123. However, after study the consensus of the Committee was that third tier toxicological testing should best be done by individual companies or groups of chemical companies testing together (for example, through the Chemical Manufacturers Association in the United States). Each chemical company would want full control of the toxicological testing, because they bear the financial liability and because both the nature and the level of impurities in the product (which could also be very significant toxicologically) vary from chemical company to chemical company and are sensitive to their exact manufacturing process. Representatives of some companies, however, indicated that they would consider accepting government subsidies on the toxicological testing in exchange for starting dates earlier than normally prudent in their financial and technical analysis.

Most members on the Committee came to the conclusion with respect to commercialization timescales (Figure 2-1) that although substantial research and development efforts are in place worldwide in the chemical industry on alternative materials at the present time, implementation of regulations on CFC-11, CFC-12 and CFC-113 by governments worldwide would define the zero point on the timescale of Figure 2-1. Some committee members felt that the regulatory strategy and even nuances within the regulations would have a significant effect in determining whether the timescale was more toward the five or more toward the ten year time period for full-scale commercialization. Certainly international agreements could have major impact in either direction.

To expedite application development, the Committee felt that user test quantities of FC-134a and CFC-123 should be made available to the industrial

Figure 2-1
COMMERCIALIZATION PROTOCOL



GO/NO-GO DECISION
 ^ |
 This Figure presented to the Committee by Luther C. Chien of E. I. DuPont de Nemours & Company

users immediately and helped the Environmental Protection Agency staff locate companies with current capabilities to deliver quantities in the ten to twenty thousand pound range within the United States and in Japan where several companies (Appendix E) can currently provide such quantities of CFC-123.

With respect to timing, it is surely true that unfavorable toxicological testing results or manufacturing problems with primary candidates, for example FC-134a and CFC-123, could cause a significant delay before other compounds were in place. It should, however, be clearly understood that the major reasons the Committee picked FC-134a and CFC-123 as leading candidates is that acute testing for both FC-134a and CFC-123 and subchronic (tier 1 and 2 - see Appendix B) testing for CFC-123 has been completed and development work and several patents for larger scale (but not commercially viable) syntheses exist for these compounds. This sets them apart from the bulk of fluorocarbon, hydrogen-containing fluorocarbon and chlorofluorocarbon materials considered by the Committee. Early analysis by the Committee, however, revealed that the toxicological testing was such a time limiting factor that the increase in time for selecting a material unscreened for toxicology (acute and subchronic) and perhaps even without pilot plant experience could be as little as six months to twelve months. As will be discussed later, there are almost no toxicological data or technical performance property data on many known fluorocarbon materials that would appear to have the physical properties necessary for use as substitutes.

A major contribution of this international committee has been to identify a large number of predominantly fluorine-containing compounds of promise for substitution in applications of currently manufactured chlorofluorocarbons, particularly CFC-11, CFC-12, and CFC-113. Following this Executive Summary these compounds are listed in three categories: Category A substitute chemicals which are primary candidates chosen to facilitate rapid implementation of alternatives; Category B substitute chemicals are secondary candidates (standby candidates), most of which are hydrogen-containing fluoroethanes and fluorochloroethanes; Category C substitute chemicals are

newer compounds and in some cases novel compounds. Category C substitute chemicals are newer compounds and in some cases novel compounds. Category C has two subclasses: a) hydrogen-containing fluorocarbons and b) perfluorocarbons and their derivatives. Details of the classification system will be discussed in Section 4. It should be noted that criteria for selecting many of the alternative materials was that at least one hydrogen be available for attack by OH radicals and/or only fluorine present as a halogen in the compound (Appendix G). It was recognized that non-hydrogen containing materials may be significant "greenhouse" gases.

Of primary importance is the Committee finding that it will be indeed possible to develop, at a moderately higher to substantially higher cost, substitutes for current chlorofluorocarbons in the event that FC-134a and CFC-123 fail for some reason. As stated before, these newer materials may be only six months to a year behind on the Figure 2-1 timescale if all committee recommendations are followed. The problem is simply that very few have been screened even for acute and subchronic toxicity and, in most cases, little more is known of their physical properties than boiling points and melting points. Essentially nothing is known about, for example, their refrigeration performance or solvent properties. In most cases, even basic thermodynamic properties are not known for these new fluorocarbons (Appendix G). It should be explained that the reason that new fluorocarbons and chlorofluorocarbons have not been screened for application in the CFC industry is that producers have known for years, with respect to the Swarts technology that their new materials would not be performance-cost competitive for such applications. Most are also manufactured by processes that would deliver these materials at a minimum of \$11.00 per kilogram and often up to \$45 or \$65 per kilogram (Appendix J).

During the course of the second meeting of the Committee, DuPont presented price projections through their committee representative which forecast cost ranges (Table 2-1) which surprised some of the committee members. These costs were said to be projections for full-scale production

TABLE 2-1. ADDITIONAL DUPONT DATA ON NEWER CFC CHEMICAL SUBSTITUTES

Chemical	Estimated Price ^a	
	\$/kg (\$/lb)	Comments
CFC-123	2.8-5.6 (1.25-2.50)	Blowing agent.
FC-134a	4.4-8.8 (2-4)	Refrigerant.
CFC-141b	2.2-4.4 (1-2)	Same as 142b.
CFC-142b	—b	Potential blowing agent or refrigerant but not used by itself because it is flammable.
CFC-122	NA	BP=71.9°C, high for a solvent, higher energy costs, more aggressive than CFC-132b.
CFC-123a	NA	Higher cost than CFC-123 and less attractive as a foam blowing agent.

NA = not available

a = In 1987 dollars. This price represents the price at full-scale production. Introductory prices may be as high as ten times these prices.

b = Currently commercial by Pennwalt Corporation.

some eight to ten years out and obviously project extremely high yield syntheses for such compounds as FC-134a and CFC-123. Should the worldwide chemical industry be as successful as this table forecasts, the prices are probably low enough to preclude materials made by other fluorination and conventional synthesis technology from competing in the new alternative materials market. Compounds in this table would be produced through modifications of Swarts technology.

The Committee listened to presentations from several user industry representatives and came to the conclusion that new prices for substitutes could be effectively borne in most applications by the users except in the very cost competitive flexible and rigid foam-blowing applications where other nonfluorocarbon materials and other technology could supplant CFC-11 and CFC-12. It has been pointed out that CFC-22 would be an adequate substitute in rigid foam sheets but would not have the diffusion stability for most foam boardstock applications (Appendix C). The Committee heard from the users a strong preference for FC-134a as a "drop-in" for refrigeration applications (requiring little modification of air conditioning units) for mobile air conditioning over CFC-22. This was a particularly strongly held preference of the automobile manufacturers. The Committee considered the lack of a known lubricating oil (which would probably be a fluorocarbon in this instance) compatible with FC-134a applications to be a problem likely to find a solution within a six-month period by any one of several companies.

The Chlorofluorocarbon Chemical Substitutes International Committee unanimously felt that immediate strong measures should be undertaken by all countries to stimulate conservation measures which lead to slower and lower volume releases of chlorofluorocarbons and believes that accomplishments can be made in this regard in almost all applications.

The Committee noted that the timescale for implementation of alternative chemicals which impact the environment is five to eight years whereas significant reductions can be made immediately through conservation efforts. In

view of the fact that CFC-113 has application in a broad spectrum of uses and only in twenty to thirty percent of these applications is there an acceptable alternative (see Section 3, Findings), the Committee favored an approach to continue the use of 113. Some committee members felt that industrial cleaning operations may not make sufficient attempts to control the emission of CFC-113 because the price is so low that recovery is not always economic. Significant improvements can be made by upgrading old cleaning equipment and improving work practices. Thus, the price could be artificially increased to make economically attractive conservation and recovery from exhaust systems or alternatively one could legislate against emissions (this was considered less effective). At the same time a vigorous research effort to synthesize and develop alternative chemicals to replace CFC-113 should be funded by the federal government. The Committee, some of whom have consummate knowledge of high-performance chemical fittings, felt that major advances could be made (Appendix I) in retaining chlorofluorocarbons in mobile air and other air conditioning applications; and that a cost for higher pressure fittings of about twenty to forty dollars per unit was very tolerable. Further, the Committee recommends strongly economic incentives to expand the use of the already commercially available CFC-22 (which requires a higher operating pressure).

It should be clearly understood by all reading this report that through the time of completion of third tier toxicology (Appendix B) and the construction of chemical plants with full-scale production capabilities, leading replacement candidates (FC-134a and CFC-123 included) could fail suddenly as replacements for these or other reasons. It is strongly recommended therefore by this Committee that the EPA organize at least annual review sessions of a committee with expertise such as the one now assembled to assess the progress of industry during the proceeding year and update recommendations concerning the most promising backup candidates to assure backup capability. Society simply cannot afford to be without alternative CFC substitute materials in the face of the mounting scientific evidence that there is indeed a strong possibility of major long-term consequences (some of

the current compounds have lifetimes of one hundred years in the atmosphere) from chlorofluorocarbon stratospheric buildup.

The Committee found that there is very little knowledge of the atmospheric chemistry of new alternative compounds other than generalizations which apply to groups. The Committee has found even less knowledge concerning the ultimate fate in the environment of such species as FC-134a (see Figure 2-2) (Appendices D, F, I). It is estimated that HCl and HF contribute to acid rain but are orders of magnitude less significant than sulfuric acid. Little is known about the effect on the atmosphere and environment of products such as small concentrations of trifluoroacetic acid or partially fluorinated acetic acid and if they will be established, in fact, as breakdown products.

The Committee has determined that it is absolutely necessary that U.S. government funds be spent (and funding encouraged worldwide) at a minimum level of \$3 million per year to support research in the academic, small industry and industrial sectors focused on a number of these extremely important problems in areas where knowledge is essentially lacking. Government regulations which were designed to effectively reduce CFC-11 and CFC-12 over a period of ten years will be made at very high risk, and "safe" effective alternatives may not be available on a timescale to meet society's demands without this relatively modest funding effort. It has been pointed out (Appendix G) that it is already past time for the prudent implementation of such scientific funding. The Environmental Protection Agency has received a few proposals but it has been determined that its staff will need expert guidance in selecting which areas to fund and it may need assistance in evaluating proposals. The Chlorofluorocarbon Chemical Substitutes International Committee, if it does indeed meet annually, could provide again some of this guidance at very little extra cost. Research needs in the alternatives area should be assessed on a year-by-year basis with changing emphasis to meet new and unforeseen scientific developments in light of yearly progress. The most important research needs (Table 2-2 contains a more

TABLE 2-2. IDENTIFIED RESEARCH NEEDS

-
-
- Investigate the tropospheric chemistry of FC-134a, CFC-123, and any other very promising chemicals.
 - Establish vigorous research efforts to synthesize or find a replacement chemical for CFC-113.
 - Determine trifluoroacetic acid toxicity and breakdown products.
 - Measure or estimate the thermodynamic properties and bond energies of newer CFC chemical substitutes.
 - Investigate a variety of possible chemical compounds for replacements and fund synthesis of new chemicals.
 - Perfluorocarbons should be tested in refrigeration and foam blown thermal applications.
 - Particular investigations should be made into the applications of CF_3SF_5 and preliminary toxicity screening of CF_3SF_5 and CFC-122 should be initiated.
 - Perform applications screening and cost estimations for the newer CFC chemical substitutes.
-
-

complete list of research needs which were identified in the Committee proceedings) are:

- (I) Atmospheric chemistry studies for specific new chemicals funded by a separate budget within the EPA from general atmospheric studies;
- (II) There is a great need for funding to synthesize new materials to be evaluated for alternative chemical applications;
- (III) We must evaluate properties of new chemicals for various applications and obtain basic thermodynamic properties for such materials;
- (IV) There is also a great need to fund research determining the ultimate environmental fate of alternative fluorocarbon materials such as FC-134a and CFC-123.

In general, there is a pressing need to evaluate at least ten or so of the most likely alternative materials from the nontraditional areas of chlorofluorocarbon and fluorocarbon chemistry for applications (Appendix G). The Committee also strongly recommended that at least twenty of the more speculative alternatives be prepared in sufficient amounts and purity for acute and subchronic toxicity testing (Appendix D). We further recommended that the Committee replace yearly any of those backup compounds which fall out of contention with others so that a worldwide pool of about ten to twenty backup materials will be available. Overall, the Committee takes the view that the level of knowledge outside of Swarts chlorofluorocarbon technology for production of materials for these applications critical to societal needs is almost nonexistent and certainly no more than in the embryonic stage. Therefore we cannot overemphasize the need for funding substantial amounts of research up to the date where important atmospheric problems such as ozone depletion and the greenhouse effect are solved in a satisfactory way.

Finally, it should be noted that there will be opportunities for user groups to discuss any aspects of this report with selected members of the Chlorofluorocarbon Chemical Substitutes International Committee.

Individual summary reports by committee members are available in Appendices A through K of this report.

SECTION 3
FORMAL FINDINGS OF THE COMMITTEE

COMMITTEE STATEMENT

Long-lived CFCs, particularly CFC-11, CFC-12, and CFC-113, have been identified as potential threats to the environment. The most immediate concern is stratospheric ozone depletion, but additionally CFCs contribute to the greenhouse effect.

Society needs chemicals to replace these CFCs in their many valuable uses such as air conditioning, refrigeration, industrial cleaning, and building insulation. Substitutes such as FC-134a and CFC-123 have been identified that appear capable of meeting many of these needs. These chemicals are expected to present a much lower risk to stratospheric ozone depletion potential and greenhouse warming than the chemicals they replace. We have developed a list of candidate materials, should they be needed, for further investigation.

We recommend that governments around the world design regulations which create strong incentives for commercialization of safe substitutes for CFCs that deplete stratospheric ozone. Since society cannot afford to be without substitute chemicals, governments should also sponsor research to reduce technical uncertainty and to enhance knowledge of chemical substitutes, particularly research into those chemicals that are not now under active consideration by chemical companies. Additionally, we strongly support immediate implementation of conservation measures to reduce emissions from existing chlorofluorocarbon applications. (Committee members are listed in Table 3-1.)

TABLE 3-1. COMMITTEE MEMBERS

Dr. R.E. Banks
The University of Manchester
Institute of Science and Technology
Manchester, England

Professor Joseph Borzelleca
Medical College of Virginia
Virginia Commonwealth University
Richmond, Virginia 23298

Dr. Luther C. Chien
E.I. duPont de Nemours & Co., Inc.
Wilmington, Delaware 08023

Professor Darryl D. DesMarteau
Hunter Chemistry Laboratory
Clemson University
Clemson, South Carolina 29634

Professor Nobuo Ishikawa
F&F Research Center
Tokyo, Japan

Professor Richard J. Lagow, Chair
Department of Chemistry
The University of Texas
Austin, Texas 78712

Dr. J. Donald LaZerte
Industrial Chemical Products Division
3M Company
St. Paul, Minnesota 55144

Professor John L. Margrave
Rice University
Houston, Texas 77251

Dr. Martin Robinson
Allied-Signal, Inc.
Buffalo, New York 14210

Professor Dr. Herbert W. Roesky
Universitat Goettingen
Goettingen, West Germany

(Continued)

TABLE 3-1. COMMITTEE MEMBERS (Continued)

Dr. Eugene Stump, Consultant
Gainesville, Florida 32605

Andrew J. Woytek
Air Products & Chemicals, Inc.
Allentown, Pennsylvania 18105

Dr. Masaaki Yamabe
Ashai Glass Co., Ltd.
Yokohama, Japan

JOINT COMMITTEE - U.S. EPA STATEMENT

The U.S. Environmental Protection Agency convened a panel of internationally recognized chemists, engineers, and toxicologists for advice on alternatives to long-lived chlorofluorocarbons that have the potential to deplete stratospheric ozone.

This panel, composed of experts from both industry and academia, explored questions of technical and economic feasibility as well as safety of new chemical compounds that are less harmful to stratospheric ozone. The panel, chaired by Dr. Richard Lagow from the University of Texas, drew both on the results of current research and on their considerable knowledge. Panel members were from several countries including the United States, Japan, the United Kingdom, and the Federal Republic of Germany.

The currently used chlorofluorocarbons CFC-11, CFC-12, and CFC-113, all have long atmospheric lifetimes. Their projected increased use would deplete stratospheric ozone, increasing the amount of ultraviolet radiation reaching the earth's surface. The Environmental Protection Agency's risk assessment contends that continued growth in the use of these chemicals could result in large increases in the incidence of skin cancer and cataracts, suppression of the immune system, climatic change, deterioration of plastics, biological changes, and other environmental effects. New chemicals that are less harmful to stratospheric ozone can be employed to provide the same useful products and services, but at additional cost to consumers.

The panel concluded that it is the absence of a market for higher priced chemicals--rather than technical or environmental barriers--that is slowing commercialization of less harmful replacement chemicals. The panel recommends that governments around the world should design regulations which create strong incentives for commercialization of the new chemicals.

The panel also concluded that the most promising new chemicals--FC-134a and CFC-123--can be produced using a variety of technologies that are available throughout the world. They rejected the possibility that a monopoly could develop and predicted that these new chemicals will be competitively produced and priced. Industrial sector representatives and other panelists indicated that research on these substitutes is being actively pursued by some chemical producers worldwide.

If regulations of the existing chemicals increase the competitiveness of the alternative chemicals sufficiently, the new chemicals can be marketed, optimistically, within six years.

In addition to the principal alternative chemicals, the panel developed a list of candidate materials that might prove to be alternatives to existing CFCs.

Experts on the panel estimated that new chemicals can be provided at prices some users can afford. Representatives from the automobile and refrigeration industries expressed a preference for FC-134a as an alternative to CFC-12 (rather than CFC-22) even if it were priced several times higher than CFC-12, because these chemicals are a small fraction of total equipment cost and would require less changes in refrigeration equipment. CFC-12 costs approximately \$0.60 to \$0.70/pound in bulk quantities. E.I. DuPont deNemours & Co., Inc. announced through their panel representative that FC-134a is estimated to sell for \$2.00 to \$4.00 per pound in bulk quantities (1987 dollars) when full-scale production is achieved. DuPont expects that introductory prices of new chemicals may be significantly higher than their price at full-scale production.

However, representatives of the rigid foam insulation industry expressed concern that they could not afford major price increases for the substitutes for CFC-11. CFC-11 is priced at approximately \$0.60/pound in bulk quantities

(1987 dollars) and its alternative, CFC-123, is estimated by DuPont to sell for \$1.25 to \$2.50 per pound in bulk quantities (1987 dollars) once full-scale production is achieved.

The panel identified the most promising substitutes, the likely range of cost, and the necessary time for commercial production. It also identified the necessary and desirable steps for timely chemical development, and recommended that the world governments undertake an ambitious effort to identify and screen additional chemical alternatives in case the most promising current alternatives are later found unsuitable.

SECTION 4
CLASSIFICATION OF CHEMICAL ALTERNATIVES

A three-category classification system was recommended by the Committee to aid in the review and evaluation of potential newer CFC chemical substitutes. The three categories are:

- o Category A--"Well-known" potential CFC alternatives currently being investigated.
- o Category B--Additional candidate substitutes for which substantial information exists.
- o Category C--Potential substitute compounds for which minimal or no information is presently available.

Category A compounds are shown in Table 4-1. Three of these chemicals are already commercially available. For the others, private industry is actively pursuing the research required for commercialization. The two leading candidates are FC-134a and CFC-123. Several process patents exist for these compounds, and in Japan CFC-123 is produced on a commercial scale as a chemical intermediate.

Examples of Category B compounds are shown in Table 4-2. These compounds represent those for which some toxicological data and physical properties are available.

These compounds may be acceptable for use as substitutes for certain currently used fully halogenated CFCs. Also, some of these compounds may be currently produced at an industrial/commercial scale, or processing may exist so that

TABLE 4-1. CATEGORY A COMPOUNDS

FC-134a	1,1,1,2-tetrafluoroethane
CFC-123	2,2-dichloro-1,1,1-trifluoroethane
CFC-124	2-chloro-1,1,1,2-tetrafluoroethane
CFC-141b	1,1-dichloro-1-fluoroethane
CFC-22*	Chlorodifluoromethane
CFC-142b*	1-chloro-1,1-difluoroethane
FC-152a*	1,1-difluoroethane

*Currently commercially available in the U.S.

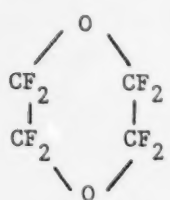
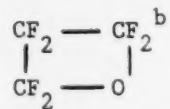
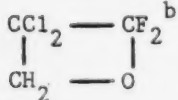
TABLE 4-2. EXAMPLES OF CATEGORY B COMPOUNDS

CF_3SF_5	Trifluoromethylsulfur pentafluoride
CFC-122	1,2,2-trichloro-1,1-difluoroethane
CFC-123a	1,2-dichloro-1,1,2-trifluoroethane

full-scale development of the chemical may be relatively easy. In general, these compounds have not been tested in specific applications which currently employ fully-halogenated CFCs.

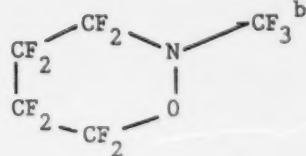
Category C compounds are those compounds that appear to be potential candidates based on relatively scant data. For these compounds, a significant amount of development work is needed in toxicological testing, physical property measurement, and applications testing. Examples of Category C compounds are given in Table 4-3. An additional listing of compounds (including some Category A and B compounds) is given in Luther C. Chien's summary in Appendix C.

TABLE 4-3. EXAMPLES OF CATEGORY C COMPOUNDS^a

Chemical Formula	BP (°C)	CAS Registry Number
$\text{CF}_3\text{CHFCH}_2\text{CF}_2\text{C}_1$	16	359-58-0
$\text{CF}_3\text{CHC}_1\text{CF}_3$	15	431-87-8
$\text{CHF}_2-\text{CF}_2-\text{CF}_2\text{C}_1$	21	CA 41 P2477b
$\text{CF}_3\text{CHFCH}_2\text{CF}_3$	-17	431-89-0
$\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3^b$	63	333-36-8
$\text{CF}_3\text{CH}_2\text{CF}_3$	-1.5	690-39-1
$\text{CF}_3\text{CHFCH}_2\text{CF}_2$	4-5	431-63-0
$\text{CHF}_2\text{CF}_2\text{CHF}_1$	11	680-00-2
$\text{CF}_3\text{CF}_2\text{CH}_2\text{F}$		677-56-5
$\text{CF}_3\text{OCF}_2\text{CH}_2\text{C}_1^b$	40	NA
$\text{CF}_3\text{OCF}_2\text{CHFC}_1^b$	NA	NA
$\text{CF}_3\text{OCF}_2\text{CHC}_1^b$	NA	NA
$\text{CF}_3\text{OCHFC}_1^b$	NA	NA
$\text{CF}_3\text{OCHFC}_1^b$	NA	NA
$\text{CF}_3\text{OCFC}_1\text{CH}_2\text{C}_1^b$	NA	NA
	23	NA
	18	NA
	NA	NA

(Continued)

TABLE 4-3 (Continued)

Chemical Formula	BP (°C)	CAS Registry Number
$\begin{array}{c} \text{CHCl} - \text{CF}_2^b \\ \quad \quad \\ \text{CHCl} - \text{O} \end{array}$	NA	NA
$(\text{CF}_3)_2\text{NOCF}_3^b$	0.6	NA
	80	NA
	47.5	NA
$\begin{array}{c} \text{CF}_3\text{N} - \text{O}^b \\ \quad \quad \\ \text{CF}_2 - \text{CF}_2 \end{array}$	-6.8	NA
$\begin{array}{c} \text{CF}_3\text{N} - \text{O}^b \\ \quad \quad \\ \text{CF}_2 - \text{CFCl} \end{array}$	30	NA
$\begin{array}{c} \text{CF}_3\text{N} - \text{O}^b \\ \quad \quad \\ \text{CF}_2 - \text{CCl}_2 \end{array}$	63	NA
$\begin{array}{c} \text{CF}_3\text{N} - \text{O}^b \\ \quad \quad \\ \text{CF}_2 - \text{CFH} \end{array}$	28	NA

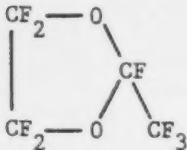
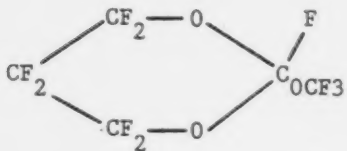
(Continued)

TABLE 4-3 (Continued)

Chemical Formula	BP (°C)	CAS Registry Number
$ \begin{array}{c} \text{CF}_3\text{CF}_2\text{N} \text{ --- } \text{O}^b \\ \quad \\ \text{CF}_2 \text{ --- } \text{CF}_2 \end{array} $	26	NA
$ \begin{array}{c} \text{CF}_2\text{Cl} - \text{CF}_2 \text{ N --- } \text{O}^b \\ \quad \\ \text{CF}_2 \text{ --- } \text{CF}_2 \end{array} $	57	NA
$\text{CH}_2\text{Cl} \text{ CF}_2\text{CF}_3$	27.2	JACS 77,3149 (1955)
$\text{CF}_2\text{Cl} \text{ CFCl} \text{ CF}_3$	34.5	JACS 73,1428 (1951)
$\text{CF}_2\text{Cl} \text{ CFCl} \text{ CH}_2\text{F}$	56	NA
$\text{CHFCl} \text{ CFCl} \text{ CHF}_2$	76	NA
$\text{CHCl}_2 \text{ CF}_2 \text{ CF}_3$	45	NA
$ \begin{array}{c} \text{CF}_2 \text{ --- } \text{CHCl} \\ \quad \\ \text{CF}_2 \text{ --- } \text{CH}_2 \end{array} $	73	JACS 83, 382 (1961)
$ \begin{array}{c} \text{CF}_2 \text{ --- } \text{CHCl} \\ \quad \\ \text{CF}_2 \text{ --- } \text{CF}_2 \end{array} $	40	NA
$ \begin{array}{c} \text{CF}_2 \text{ --- } \text{O} \\ \quad \\ \text{O} \text{ --- } \text{CF}_2 \end{array} $	NA	35818-23-6
$ \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{CF}_2 \quad \text{CF}_2 \\ \quad \\ \text{CF}_2 \text{ --- } \text{O} \end{array} $	-10	21297-65-4
$\text{CF}_3\text{OCF}_2\text{CF}_2\text{H}$	NA	2261-01-0

(Continued)

TABLE 4-3 (Continued)

Chemical Formula	BP (°C)	CAS Registry Number
$\text{HCF}_2\text{OCF}_2\text{H}^b$	NA	1691-17-14
$\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_3$	2	Zh.Org.Khim. 10,2031,1974
	8	"
$\text{CF}_3\text{O CF}_2\text{CF}_2\text{O CF}_2\text{CF}_3$	38.5	"
	41	

NA = not available

^aList of compounds provided by Professor Darryl D. DesMarteau.^bCompounds known or suspected to be toxic and therefore unlikely to be suitable as substitutes (E. Banks, N. Ishikawa, E. Stump).

APPENDIX A

SUMMARY REPORT

By:

Dr. R.E. Banks
Chemistry Department
The University of Manchester Institute
of Science and Technology
Manchester M60 1QD, England (U.K.)

May 4, 1987

GENERAL COMMENTS AND RECOMMENDATIONS

1. I recommend that conservation of current commercial CFCs (chlorofluorocarbons), CFHCs (chlorofluorohydrocarbons), FHCs (fluorohydrocarbons) and brominated analogues (Halon) be highlighted as a "must" for immediate attention by all user nations. This should apply particularly to CFC-113 ($\text{CF}_2\text{ClCFCl}_2$) in its solvent applications, and Halons 1211 and 1301 used as fire extinguishing agents. As Dr. Stephen Andersen of the U.S. EPA has explained, conservation of Halons is possible by simulating their use in fire-fighting practice exercises; and the lack of condensing systems in baths of CFC-113 was clearly indicated by Dr. Donald LaZerte. Note that a conservation approach should also apply, where practicable, to methylchloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4) because, clearly, the less organochlorine material released to the atmosphere, the better.
2. In connection with the conservation of CH_3CCl_3 , the argument may be advanced by some that since this compound has a relatively short lifetime (ca. 8 years) owing to its destruction by tropospheric hydroxyl radical, tight control of emissions is not warranted. But what happens if mankind overburdens the hydroxyl radical sink? And having raised this point, could it occur through the substitution of current CFC's 11 and 12 with hydrogen-containing compounds? Clearly, it would be prudent to insist on conservation measures being applied also to FHCs or CFHCs (e.g. FC-134a, CFC-123) if and when they replace current CFCs. Conservation clearly impacts on the magnitude of the greenhouse effect, of course.

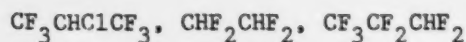
CATEGORIZATION OF SUBSTITUTES FOR CURRENT COMMERCIAL LONG-LIVED CFCs

I suggest that possible substitutes for current commercial CFC's suspected of depleting stratospheric ozone be classified as follows:

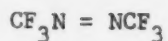
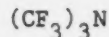
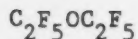
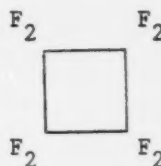
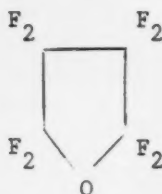
- (A) Primary Candidates. (That is, compounds containing one or more C-H bonds and the minimum number of C-Cl bonds, which have already undergone screening of one sort or another.) At present, this category contains only halogenoethanes of the CFHC (chlorofluorohydrocarbon) or FHC (fluorohydrocarbon) class; as research gets underway, candidates from other classes may be promoted to this class. Note that the CFC Committee has identified only two primary candidates so far: FC-134a ($\text{CF}_3\text{CH}_2\text{F}$; substitute for CFC-12) and CFC-123 (CF_3CHCl_2 ; substitute for CFC-11).
- (B) Standby Candidates. These have not proved as promising (for one reason or another) as Class A compounds. At present, the class comprises the halogenoethanes already identified by DuPont (in addition to FC-134a and CFC-123), namely: CFC-132b ($\text{CF}_2\text{ClCH}_2\text{Cl}$), CFC-141b ($\text{CH}_3\text{CFC}_2\text{Cl}$), CFC-124 ($\text{CF}_3\text{CHFC}_2\text{Cl}$), CFC-142b ($\text{CH}_3\text{CF}_2\text{Cl}$), CFC-152a (CH_3CHF_2), CFC-143a (CF_3CH_3), and two which I raised, namely CFC-122 ($\text{CF}_2\text{ClCHCl}_2$) and CFC-123a ($\text{CF}_2\text{ClCHFC}_2\text{Cl}$). The last two boil at 71.9°C and 28.2°C , respectively. Dr. Luther Chien stated that DuPont had rejected these on the grounds that CFC-122 has too high a boiling point when one considers the energy required for solvent recovery, while CFC-123a was too costly to manufacture as a blowing agent. His other comments were that CFC-132b would be applicable to only 20 percent of the CFC-113 market (as it is too aggressive a solvent for the remaining 80 percent, a point also made by Ishikawa/Yamabe from Japan); that CFC-141b and CFC-142b were flammable; and that CFC-142b--a potential refrigerant and blowing agent--was not "viable across the board" by itself.

(C) Newer Candidates. This class needs to be subdivided into compounds containing C-H bonds and those not containing hydrogen.

(i) H-Containing Compounds



(ii) Fluorocarbons and their Derivatives



Obviously, the advisability of releasing class C(ii) compounds will be questioned since they may well have no tropospheric "fates."

I do not feel able to support the addition of any more candidates to this class on the grounds of practicability and the known propensity for fluorinated compounds containing C-H bonds to possess anesthetic properties (see Preparation, Properties and Industrial Applications of Organofluorine Compounds [ed. REB], Ellis Horwood, Chichester, 1982, Ch 5). We also need to be aware that class C(ii) compounds can be criticized on the grounds that fluorocarbon blood substitutes containing N or O are known to be retained in vital organs. Greenhouse problems will also be raised.

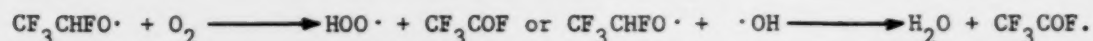
I do not feel that we should be put off testing "attractive" (especially from the synthesis viewpoint) substitutes, though. We need to seek photolabile compounds in particular.

TESTING OF POTENTIAL SUBSTITUTES

I wish to emphasize that the tropospheric fates of all potential substitutes should be determined as accurately as possible at an early stage in their assessment. We need to have a pretty good idea of what they will "rain-out" as once hydroxyl radical (predominantly, I suppose) or a related species has attacked (at, presumably, a C-H bond). I made this point several times at the two meetings, and provided photocopies of the information on my transparencies to all concerned. Also, recent relevant references to HO (and Cl) attack on halogenoalkanes were provided. The recent paper by N. Cohen and S.W. Benson (J. Phys. Chem., 1987, 91, 162-170) was circulated, so the "best" $\log k$ experimental values are available (in Tables XII and XIII, pp. 169 and 170 in that article).

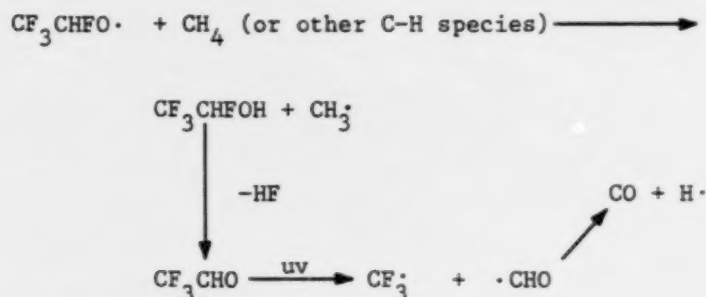
According to the literature data, FC-134a ($\text{CF}_3\text{CH}_2\text{F}$) should have a tropospheric lifetime close to that of methane (Dr. F.S. Rowland concurred), i.e. about 10 years. The first step in FC-134a's destruction is expected to be $\text{CF}_3\text{CH}_2\text{F} + \text{OH} \longrightarrow \text{CF}_3\dot{\text{C}}\text{HF} + \text{H}_2\text{O}$. The major fate of the carbon-centered radical produced can reasonably be predicted to be formation of a peroxy radical, as follows: $\text{CF}_3\dot{\text{C}}\text{HF} + \text{O}_2 \longrightarrow \text{CF}_3\text{CHF}\text{O}\dot{\text{O}}$. From there, the matter is open to speculation. One pathway, which has analogy with the mechanism proposed in Chapter 4 of Atmospheric Ozone 1985, Volume I (World Meteorological Organization Global Ozone Research and Monitoring Project; Report No. 16), NASA publication, is as follows: $\text{CF}_3\text{CHF}\text{O}\dot{\text{O}} + \text{NO} \longrightarrow \text{CF}_3\text{CHF}\dot{\text{O}} + \text{NO}_2$.

Once formed, the tetrafluoroethoxy radical may yield trifluoroacetyl fluoride vis crossed disproportionation with another radical species, e.g., hydroxyl or oxygen:



The acid fluoride will "rain out" as hydrofluoric acid and trifluoroacetic acid or photolyse: $\text{CF}_3\text{COF} \longrightarrow \text{F}\cdot + \text{CO} + \text{CF}_3\cdot$

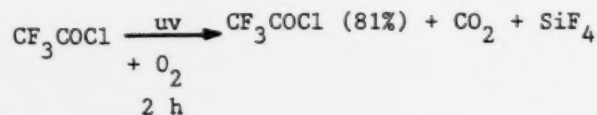
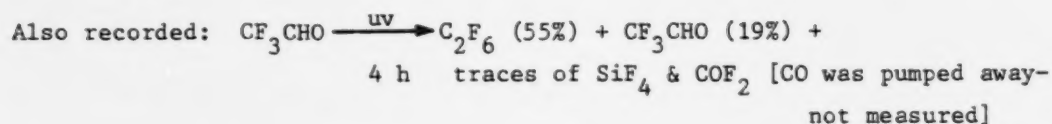
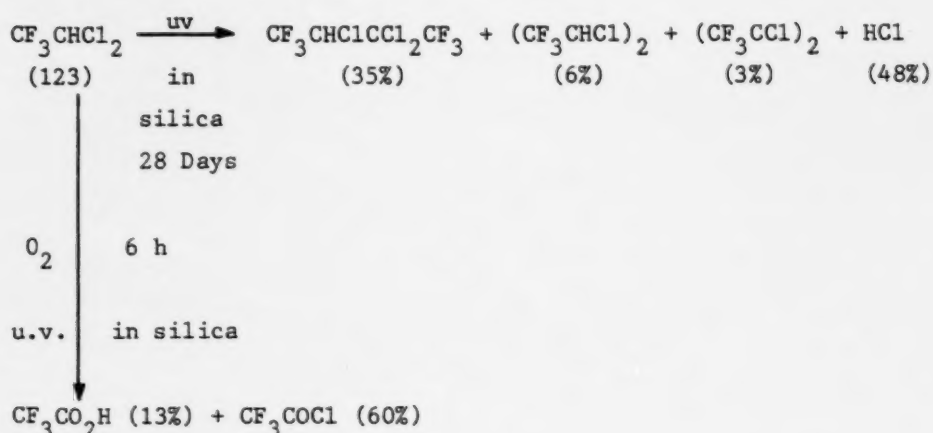
A further possibility is



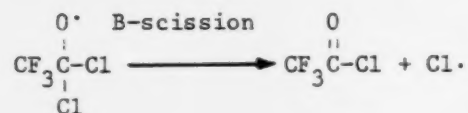
(See C. Pearce and D.A. Whytock, Chem Comm., 1971, pg. 1464.)

Either way, HF is formed--and the tropospheric chemistry of this has already been examined owing to its formation from current CFCs (see pg. 618 of Volume II of the NASA publication mentioned above); however, trifluoroacetic acid (which I predict will arise from tropospheric decomposition of both the primary candidates $\text{CF}_3\text{CH}_2\text{F}$ and CF_3CHCl_2) poses new problems which must be addressed. I cannot believe that industries (DuPont, Allied, ICI) which have already identified $\text{CF}_3\text{CH}_2\text{F}$ as a prime contender for CFC-12's place in society, have not considered the possibility that emissions will return to ground level as $\text{CF}_3\text{CO}_2\text{H}$. Surely they will have done laboratory experiments to check on this. Anderson of General Motors (Anderson, L.G., "The Atmospheric Chemistry of 1,1,1,2-Tetrafluoroethane," General Motors Research Laboratories, Warren, MI, November 10, 1980) has certainly addressed the problem and like me, points out that $\text{O}(^1\text{D})$ can also remove $\text{H}\cdot$ from FC-134a. He predicts a 6.4 year lifetime for FC-134a (see pg. 6 of his report).

Note that laboratory oxidations have involved CF_3CHCl_2 (CFC-123), $\text{CF}_3\text{CH}_2\text{Cl}$ (CFC-133a), $\text{CFCl}_2\text{CHCl}_2$, and $\text{CF}_2\text{ClCHCl}_2$ - as mentioned by M. Hudlicky in Chemistry of Organic Fluorine Compounds, Horwood: Chichester, 1976 (2nd revised edn.), pg. 199. Strangely, however, Hudlicky does not list the paper most pertinent to our discussion, namely that by R.N. Haszeldine and E. Nyman, J. Chem. Soc., 1959, 387, which records the photolysis of CF_3CHCl_2 alone and in the presence of oxygen:



The step which provides CF_3COCl is the one I used, namely:



where the oxidation is initiated by abstraction of hydrogen atom from CF_3CHCl_2 . When photodissociation of a C-Cl bond in CF_3CHCl_2 is the primary step, loss of H from $\text{CF}_3\text{CHClO}\cdot$ needs to be invoked (see pg. 391 of the Haszeldine-Nyman paper).

APPENDIX B

SUMMARY REPORT

By:

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May 8, 1987

TOXICOLOGY TESTING

Toxicological evaluation of any substitute chemical should be undertaken only after the fate (theoretical, experimental) of the new chemical in the atmosphere has been determined; that is, that it will probably not adversely affect ozone levels. The new chemical to be evaluated should be produced by the process that will be commercialized. The evaluation procedure is outlined below. Details are presented in the appendix to this paper.

A comprehensive search of the scientific literature is undertaken to identify any toxicological data. In addition, the chemical/physical/thermal properties of the candidate chemical, as well as its structure, should be made available to those conducting the evaluation. It is important that an estimate of human exposure be made; this will assist in the selection of doses for testing.

Tier 1. This initial series of tests is conducted to establish a profile of the acute effects, including signs of intoxication preceding death. These data are compared to known compounds. The approximate lethal dose (ALD) or the lethal dose₅₀ (LD₅₀) is determined. The routes of exposure include inhalation, oral and dermal. The potential dermal sensitization and the irritation potential of the test compound on ocular and dermal tissues is also determined. To minimize resources but not compromise integrity of the evaluation, only male animals need be used. If the compound is no more toxic than compounds currently used, then testing proceeds to the next phase. If the compound is more toxic than currently used materials, then movement to the next tier of testing must be rigorously supported or defended.

Tier 2. Data obtained in this phase should provide the following information: compound and dose-dependent effects (cumulative) of repeated exposure (14 and 90 days); identification of potential target organs; progression and reversibility of effects and/or lesions; fate, distribution and kinetics; developmental effects, mutagenic and potential carcinogenic effects. Tests to be performed in this phase include subchronic inhalation; developmental effects; absorption, distribution, biotransformation, elimination and kinetics; and a complete battery of genetic toxicity tests.

The data generated in this phase are critically reviewed to determine the presence of dose-dependency, reversibility and severity of effects, as well as mutagenicity and potential carcinogenicity. A conclusion concerning the limits of human exposure (acceptable exposure limits) can be made. Mutagenic and potential carcinogenic effects are interpreted in light of toxicity. Comparative data on the absorption, distribution, biotransformation, excretion and kinetics will provide insight into the toxicity observed and the appropriateness of the animal model used. The decision to proceed to Tier 3 testing should be based on a combination of factors: the data obtained from Tier 2 studies, and the apparent acceptability of the chemical by the users rendering its further development economically feasible.

Tier 3. Data obtained in this phase should provide the following information: compound and dose-dependent effects of chronic (lifetime) exposure and the reversibility of the effects; carcinogenic potential; effects on reproductive performance; target organ(s) of toxicity; potentially unique toxicities and environmental effects. Tests to be performed in this phase include chronic inhalation (chronic toxicity/carcinogenicity); chronic oral (chronic toxicity/carcinogenicity, if indicated), multigeneration reproductive

toxicity (2 generation), and appropriate special tests (cardiac sensitization, neurotoxicity, immunotoxicity, and environmental impact).

All the toxicological data generated (from all phases) are critically reviewed to determine the presence of compound and dose dependency, reversibility, and severity of toxic effects. Special consideration must be accorded the effect of the exposure on tumor induction, since a primary, but not an exclusive, concern is the issue of carcinogenicity. The effects on reproductive performance should be contrasted with developmental effects observed in Tier 2. Analysis of all these data will result in the identification of safe exposure conditions (exposure conditions that will not result in adverse health effects). The decision to fully commercialize the substitute chemical can then be made.

The decision to proceed or not with the development of the chemical should be based primarily, but not exclusively, on the toxicological evaluation. Atmospheric effects and economic considerations (including cost of production, commercialization, acceptance by users and consumers) must also be accorded high priority.

APPENDIX

Tier 1

This is the phase of acute toxicity testing and includes the following: acute toxicity following inhalation, oral and dermal exposures; eye and skin irritation and skin sensitization studies. The studies and the approximate costs in time and volume appear on Table 1.

The procedures used for these studies are fairly standardized (e.g. U.S.F.D.A.'s Toxicological Principles for the Safety Assessment of Direct Food Additives and Color Additives Used in Food ("Red Book")). Minor modifications may be made in various laboratories but the tests are conducted generally in accordance with these protocols.

Tier 2

This is the pre-chronic phase of toxicity testing and includes subchronic inhalation (14 and 90 days); developmental toxicity; absorption, distribution, biotransformation, elimination and kinetics and a complete battery of genetic toxicity tests. The costs, time and volume of material required for these studies are also presented in Table 1. The protocols used are standardized (for example, OECD guidelines). Here, also, minor modifications may be made. The 14-day study is usually conducted to identify target organs and to help to establish dose levels for the subchronic (90-day study). Subchronic inhalation studies should be conducted in male and female rats. As noted earlier, the preliminary repeated exposure study (14 or possibly 28 days) should be conducted in male rats only, since the study is to identify exposure conditions. Animals should be exposed at least 6 hours/day, 5 days/week.

Although the ideal situation would be to have animals exposed 90 consecutive days, this is an extremely difficult situation and the procedure generally used internationally is that exposure be 5 to 6 hours per day, 5 days per week. Animals should be observed at least twice daily with an interim of 5 hours between observations. The clinical evaluations (chemistries, hematology, urinalysis) should be conducted on 10 animals/sex/level after 4 weeks of exposure and then on all survivors at 13 weeks of exposure. All animals that die or are sacrificed are subjected to a thorough pathological evaluation (gross and histologic). The appropriate data include body weight, food consumption, clinical chemistry, hematology, urinalysis, gross and histopathology. All the data are subjected to appropriate statistical analysis and biological and statistical interpretations made. The mutagenicity/potential carcinogenicity testing should involve the Ames test (with and without activation), Chinese hamster ovary, cell transformation, unscheduled DNA synthesis, and other appropriate tests that are available in the laboratory.

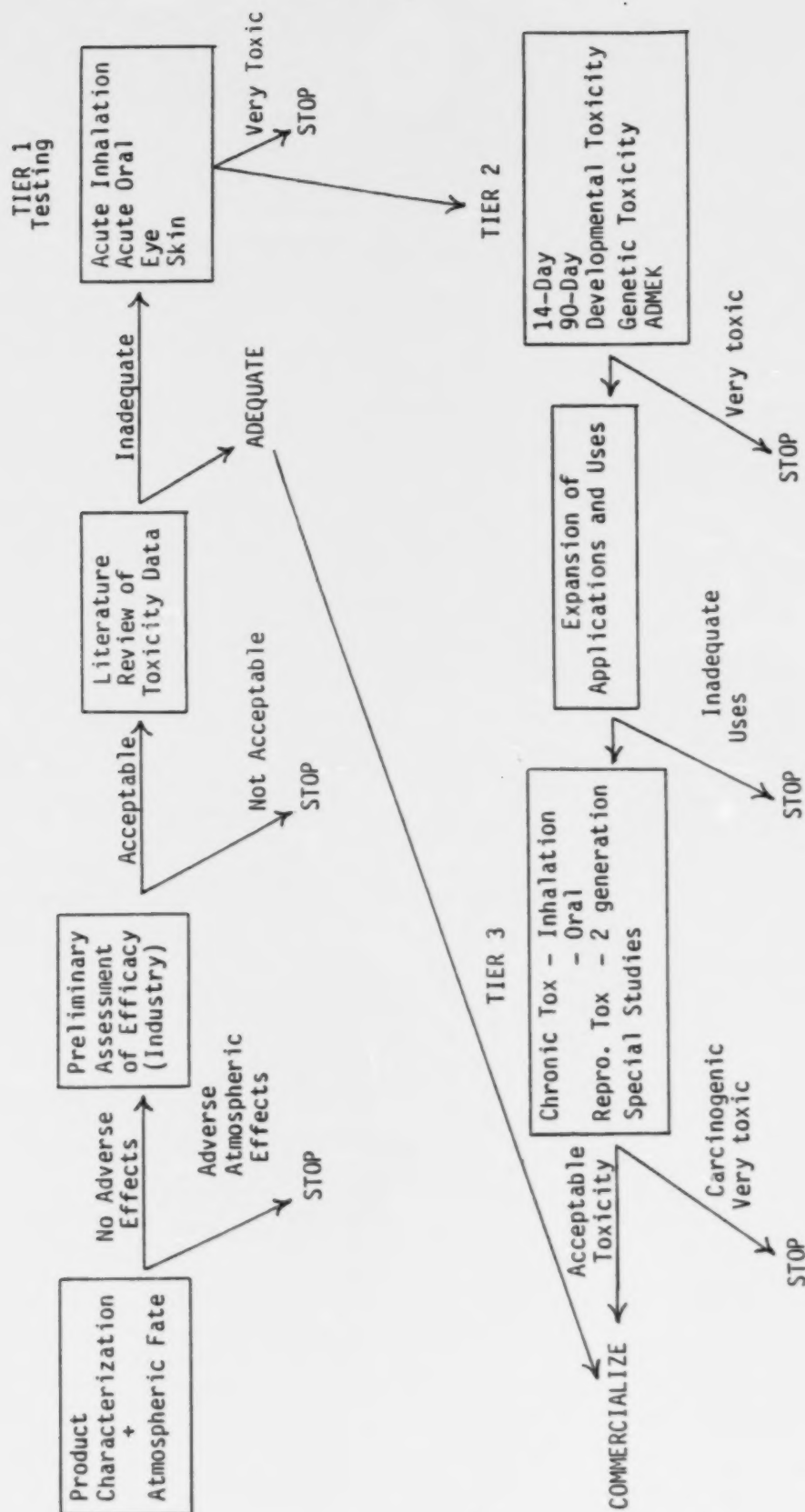
The issue of reversibility should be addressed during these studies. A recommendation is that at the end of the exposure period, at least 5 animals/sex/treatment level are returned to control conditions; that is, no exposure to the test material for one month, then a thorough clinical evaluation followed by gross and histopathological evaluations.

Tier 3

This is the chronic toxicity (lifetime exposure/carcinogenicity) phase and includes lifetime exposure (from moment of conception, in utero), effects on reproductive performance and an assessment of special toxicities. The costs, time and volume of material required for these studies are also presented in

Table 1. The doses to be used for the inhalation chronic toxicity/carcinogenicity study are based on the results of the subchronic inhalation study. The doses to be used in a chronic oral toxicity/carcinogenicity study will have to be based on a 28- or 90-day pre-study. The doses to be used for the multigeneration/reproduction study should be based on an analysis of the subchronic data as well as the data from the developmental toxicity study. All special tests that are conducted should use doses that are relevant (that is, either related to the anticipated human exposure or to those used in the 90-day or lifetime study). All responses evoked should be compound and dose dependent for appropriate toxicological analysis.

Should the candidate chemical result in an increase in the development of tumors, the use of appropriate risk assessment should be considered. The need for the model and the choice of a model should be made only after the data have been thoroughly and critically reviewed by competent toxicologists.



Requirements to be determined by EPA.

A MODIFICATION OF THE TOXICITY STUDIES CONDUCTED BY E. I. DU PONT CO.

FOR ALTERNATIVE FLUOROCARBONS

<u>Haskell Lab Test</u>	<u>Description</u>	<u>Cost^a/</u>	<u>Time^a/</u>	<u>Volume^a/</u>
ALD/LD50 (oral)	Lowest lethal dose or calculated dose producing 50% mortality	\$1,000-\$2,000	1 month	1-10 lbs.
ALC/LC50 (inhalation)	Lowest lethal concentration or calculated concentration producing 50% mortality	\$10,000	1 month	1-10 lbs.
ALD/LD50 (dermal)	Lowest lethal dose or calculated dose producing 50% mortality after dermal application	\$3,000	1 month	1-10 lbs.
Skin Irritation	Ability of compound to produce irritation when applied to the skin of rabbits	\$300	1 month	< 1 lb.
Skin Sensitization	Ability of compound to produce an allergic response in guinea pigs after repeated application	\$3,700	1 month	< 1 lb.
Eye Irritation	Ability of compound to produce ocular damage to the rabbit eye	\$500	1 month	< 1 lb.
Subacute Inhalation	Two-week study by the inhalation route to determine cumulative toxicity potential and/or target organ	\$55,000	6 months	2,000 lbs.
Subchronic Inhalation	90-Day study to determine subchronic toxicity potential by the inhalation route	\$180,000	1 year	10,000 lbs.

<u>Haskell Lab Test</u>	<u>Description</u>	<u>Cost^{a/}</u>	<u>Time^{a/}</u>	<u>Volume^{a/}</u>
Chronic Inhalation	Two-year study to determine chronic toxicity and/or carcinogenic potential in one species (rat or mouse)	\$1,200,000	4 years	80,000 lbs.
Chronic Oral	One- or two-year feeding/gavage study to determine chronic toxicity and/or carcinogenic potential in one species (rat or mouse)	\$880,000	2-4 years	80-100,000 lbs.
Developmental Toxicity Rats	Effect of compound on pregnant rats or rabbits and their offspring	\$125,000	6 months	200-300 lbs.
Reproductive Toxicity 2-generation	Effect of compound on ability of rats to successfully mate and reproduce	\$180,000 (oral) \$300,000 (inhalation)	2 years	50-80,000 lbs.
Cardiac Sensitization	Ability of compound to sensitize the beagle heart to exogenous epinephrine	<u>b/</u>	1-6 months	1-10 lbs.
Mutagenicity tests (Ames test, Cho test etc.) as gas	Gene or point mutations, Chromosome aberrations, DNA damage and repair, and sister chromatid exchange as well as other tests (14 more)	CHO/SCE \$ 20,000 CHOCA \$ 18,000 CHOHBrT \$ 22,000 Ames \$ 5,000	1-6 months	1-10 lbs.
ADME + Kinetics			1 year	< 100 lbs.
Special Tests	Neurotoxicity (including behavior), immunotoxicity		1 year	< 100 lbs.
	Environmental Impact - aquatic		1 year	< 100 lbs.

a/Approximate

b/Cost will depend on the laboratory --- whether or not they routinely conduct these tests.

APPENDIX C

SUMMARY REPORT

By:

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May 21, 1987
Revised August 5, 1987

CHEMICAL SUBSTITUTES FOR FULLY
HALOGENATED CHLOROFLUOROCARBONS

Summary of DuPont Input to CFC
Chemical Substitutes Committee

PREFACE

This report is submitted by Dr. L. C. Chien of E.I. Du Pont de Nemours and Company, Inc. to summarize Du Pont's input to the Chlorofluorocarbon Chemical Substitutes Committee on which he served. The subject committee, which was chaired by Dr. Richard J. Lagow of the University of Texas at Austin, was assembled by the Radian Corporation under contract to the U.S. Environmental Protection Agency to identify the most promising substitutes for CFCs-11, -12, and -113 and to establish the factors which influence commercialization of these substitutes. The references to Committee recommendations reflect majority opinions reached during Committee workshops conducted on February 19-21 and April 22-24, 1987 and do not necessarily reflect the views of individual Committee members or the institutions they represent.

DU PONT POSITION ON CFC SUBSTITUTES

- o Industry will make available several promising CFC chemical substitutes which can be developed into commercial products within five to eight years after market demand has been established, subject to:
 - successful toxicity testing
 - successful process development research
 - successful user application testing
 - acceptance by users
- o The best incentive to rapid commercialization of substitutes is to allow the private sector to pursue their own alternatives development with government encouragement by:
 - early clarification of regulatory approach in U.S.
 - support of atmospheric research to further define ozone depletion and greenhouse potentials
 - prompt approvals by necessary regulatory agencies
 - working with users to encourage acceptance
- o Because the private sector must assume liability for any products that are commercialized, all toxicity and application testing should remain in the private sector.
- o Unilateral regulatory action by the U.S. will not effectively address the global ozone depletion and greenhouse problems. A global protocol is required to resolve these issues.
- o Unless a clearly defined global protocol on the ozone depletion and greenhouse issues is implemented, any restrictions on existing CFCs will place U.S. companies at a competitive disadvantage in domestic and export markets.
- o FC-134a ($\text{CF}_3\text{CH}_2\text{F}$) and CFC-22 (CHClF_2) could potentially replace CFC-12 in most applications.
- o CFC-123 (CHCl_2CF_3) or CFC-141b (CCl_2FCH_3) could potentially replace CFC-11 in most applications, but barriers of cost and flammability, respectively, must be overcome.
- o None of the alternatives screened thus far have shown the potential to replace CFC-113 in all or even most of its cleaning agent applications; conservation is strongly recommended.

I. INTRODUCTION

Photochemical models of the stratosphere suggest that continued growth in the emissions of fully halogenated chlorofluorocarbons might lead to depletion of the earth's stratospheric ozone layer. The CFC Chemical Substitutes Committee, composed of representatives from the chemical industry and academia (see Appendix A), was assembled by the Radian Corporation under contract to the U.S. Environmental Protection Agency to explore the potential alternative chemicals for the three chlorofluorocarbons with the highest estimated potential for depleting ozone based on their projected increased use: CFCs -11 (CCl₃F), -12 (CCl₂F₂), and -113 (CCl₂FCClF₂).

Since the stratospheric ozone layer protects the earth's surface from harmful levels of ultraviolet radiation, domestic and international policy makers are considering action to limit the use of these CFCs. Such action must be carefully planned since these compounds play a major role in our society. Their low cost, low toxicity, nonflammability, heat transfer characteristics and compatibility with materials of construction have led to their widespread use as cleaning agents in the metal working and electronics industries, as working fluids in refrigeration and air conditioning, and as blowing agents in the manufacture of plastic insulation, packaging and cushioning foams.

Reduced availability of the existing CFCs without suitable replacements could have adverse economic and social impacts; therefore, the Committee was established to:

- o identify the most promising substitutes for these compounds in terms of technical and economic feasibility and product safety;
- o estimate cost and time to commercialize these substitutes;
- o specify necessary market conditions for commercialization.

This report summarizes information presented by Du Pont during workshops which the Committee conducted on February 19-21 and April 22-24, 1987 to review these topics. Section II reviews key factors affecting CFC chemical substitute commercialization. Sections III through VIII review boundary characteristics required and suggested alternatives for the current CFC-11, -12 and -113 applications in flexible and rigid foams, refrigeration, mobile air conditioning and cleaning agents. This report makes no attempt to quantify current usage of the existing CFCs.

Appendix A provides a listing of Committee members and consultants from the CFC user and scientific communities. Appendix B lists compounds suggested by Committee members as possible substitutes for which insufficient data exists to assess commercial potential.

II. FACTORS AFFECTING COMMERCIALIZATION OF CFC CHEMICAL SUBSTITUTES

IIA. Ozone Depletion and Greenhouse Potentials

Shortly after the ozone depletion hypothesis was proposed in 1974, several CFC producers independently initiated programs to develop chlorofluorocarbon alternatives to the suspect fully halogenated CFCs, especially CFC-11 and CFC-12. By 1980, large research investments by CFC producers had identified a number of candidate alternatives and outlined the major deficiencies or technical stumbling blocks associated with each. A particular deficiency was the projected higher cost for some of the most promising products. At about this time, scientific and regulatory concern over CFCs began to decrease. This, in combination with market surveys of CFC users which indicated little interest in more expensive alternatives, led to a de-escalation of effort in 1980.

When concern was expressed in 1985 and 1986 over potential ozone depletion and greenhouse warming effects of continued growth in fully halogenated CFCs, CFC producers reinitiated their efforts to develop alternative products by building on their previous research. Since ozone depletion and greenhouse potentials are major criteria for deciding whether a potential substitute warrants further consideration, a brief discussion of these subjects is warranted.

The uncertainties in the relative ozone depletion potentials (ODP) and greenhouse potentials (GP) and the advantages of short atmospheric lifetimes are often overlooked. Atmospheric lifetime is a dominant factor in estimating ozone depletion and greenhouse potentials. Fully-halogenated CFCs are primarily lost by photolysis in the stratosphere while hydrogen-containing CFCs are primarily destroyed by reaction with hydroxyl radicals in the troposphere. This tropospheric loss mechanism results in much shorter (but very uncertain) atmospheric lifetimes for the hydrogen-containing compounds which in turn leads to small but very uncertain ozone depletion and greenhouse potentials. These shorter lifetimes offer the additional advantage over fully-halogenated CFCs that, if scientists discover some unexpected effect due to the potential alternatives and emissions were decreased, the atmospheric concentrations of these compounds would decay rapidly and environmental effects would be minimized.

Table II-1 shows calculated values of atmospheric lifetime, ODP and GP for the existing CFCs and several possible substitutes. Atmospheric lifetimes listed are those reported by Wuebbles in 1983 and values calculated by Du Pont in April 1987.

Don Wuebbles of Lawrence Livermore National Laboratories (LLNL) calculated ODP values using a photochemical model of the atmosphere and referenced these values to CFC-11. The calculated ozone depletion at steady-state for an annual emission rate X (in mass units) of compound Y is divided by the calculated ozone depletion at steady state for an annual emission rate of X of CFC-11 to determine a relative ozone depletion potential for compound Y . Note that FC-134a has an ozone depletion potential of zero since the compound contains no chlorine.

The GP values were calculated using the Du Pont 1-dimensional radiative convective model and are referenced to CFC-12 which has been arbitrarily assigned a GP value of one. These values are critically dependent on atmospheric lifetime and the strength and location of infrared absorption bands in the 8 to 13 micron region. For the hydrogen-containing compounds, lifetimes are controlled by destruction rates in the troposphere; these rates are determined by the atmospheric hydroxyl radical concentrations and the rate constants for reactions between the fluorocarbons and hydroxyl radicals. Atmospheric concentrations at steady state came from the DuPont 1-D chemistry model using the rate constants for reactions of OH with each chlorofluorocarbon that were supplied by Bob Hampson, NBS. The IR absorbance data were measured by Du Pont in April 1987.

Du Pont believes the infrared band strength measurements are accurate to within about 30% and that uncertainty in calculated hydroxyl radical concentrations is at least a factor of two. Dr. Hampson advised Du Pont that rate constant uncertainties ranged from +/- 30% to +/- a factor of 3. Thus, the overall uncertainties in calculated GPs are dominated by uncertainties in the calculated atmospheric lifetimes which are about +/- a factor of 3.

Note that Du Pont has not yet measured IR absorption for either CFC-141b or CFC-123 and has only estimated upper limits to the GPs for these species. Du Pont is in the process of obtaining these measurements and will report these values when the work is complete.

TABLE II-1
OZONE DEPLETION AND GREENHOUSE POTENTIALS

SPECIES CFC-	WUEBBLES LIFETIME (YEARS)	DU PONT LIFETIME (YEARS) *	RELATIVE OZONE DEPLETION POTENTIAL **	RELATIVE GREENHOUSE POTENTIAL **
11	64		1.0	0.40
12	108	145	0.9	1.00 *
113	88		0.8	0.3 to 0.8
22	28	19	0.05	0.08 *
123		2 ***	<0.05 ***	<0.1
124		8	<0.05 ***	0.06 *
132b		5	<0.05 ***	0.03 *
134a		10	0	0.08 *
141b		5 ***	<0.05 ***	<0.1

* Values calculated using Du Pont 1-D model and Du Pont measurements of IR absorption.

** On a mass per mass basis.

*** Values estimated by Du Pont using best available data.

Reference: Wuebbles, D.J. "Chlorocarbon Emission Scenarios: Potential Impact on Stratospheric Ozone," J. Geophys Research, 88, 1433-1443, 1983.

IIB. Screening of Potential CFC Chemical Substitutes

Potential CFC chemical substitutes were initially screened versus these characteristics:

- 1) Ozone depletion potential
- 2) Greenhouse potential
- 3) Local Photochemical Effects
- 4) Potential Effects of Decomposition Products
- 5) Expected Toxicity - Acute, Subchronic, Chronic
- 6) Flammability
- 7) Physical / chemical properties needed for end-use application
- 8) Compatibility with end-use equipment materials of construction
- 9) Estimated product cost to end user

The CFC application screening characteristics for flexible and rigid foams, refrigeration, mobile air conditioning and cleaning agent applications were based on existing manufacturing equipment and practices to minimize the need for changes in the end-use industries, thereby permitting faster commercialization of the CFC alternatives. These boundary characteristics and the alternatives which best fit them are summarized in Sections III through VI of this report.

It should be recognized that any alternative compound to the existing CFCs is likely to be more expensive and/or involve the assumption of higher risk by the user due to flammability or toxicity of the alternative. The alternative compounds reviewed in the May 1986 Radian report are all projected to be more expensive than the existing CFCs due to higher raw material costs and high investment required to manufacture these compounds commercially. Since these compounds are still being developed, their eventual market price may be affected by additional factors including disposal costs for undesired byproducts, poor conversion or corrosion problems. If the alternative chosen by the user poses hazards which are not encountered using the existing CFCs, the user may have to revise equipment or work practices to minimize the risk associated with making this change.

The proposed substitutes seem to have minimal potential environmental impact. The ozone depletion potentials of the substitute compounds are significantly smaller than those of the fully halogenated CFCs. The greenhouse potentials of the potential substitutes also are significantly smaller than those of the compounds they might replace. The atmospheric lifetimes of the compounds are long enough so that they would not contribute to local photochemical pollution.

Decomposition products of the potential alternatives for the fully halogenated CFCs would not be expected to contribute to environmental hazards (e.g. acid rain) because their atmospheric concentrations would always remain very small. Consider, for example, a compound with annual emissions equivalent to 1986 emissions of CFC-11 and CFC-12. Atmospheric mixing would result in a steady-state tropospheric concentration of about 33 parts per trillion. The decomposition products corresponding to this 33 part per trillion tropospheric CFC concentration would have a very small atmospheric acid contribution when compared to the global acid contribution of fossil fuel combustion.

IIC. Commercialization of CFC Chemical Substitutes

Before commercialization of substitutes is discussed, it must be understood that substitutes are only being considered due to concerns over environmental effects of current CFCs and potential regulations which may restrict their use. CFCs -11 and -12 have been on the market for more than 50 years and CFC-113 for more than 30 years. Their low cost, low toxicity, nonflammability, heat transfer characteristics and compatibility with materials of construction have led to their widespread use as working fluids in refrigeration and air conditioning, as blowing agents in the manufacture of plastic insulation, packaging and cushioning foams, and as cleaning agents in the metal working and electronics industries. All substitutes identified have clear disadvantages in cost, toxicity or performance when compared to the existing CFCs. Therefore, it appears that markets for the substitutes will develop only if changes in cost or availability of the existing CFCs force that development.

In developing substitutes, potential producers and users must decide whether they want to risk the required R&D and capital expense in view of the uncertainties of toxicity, performance, cost and future regulations. Before producers commit capital for production facilities, time and resources are needed for producers to complete toxicity studies and users to qualify new materials for their applications. Producers face the risk that competitive manufacturers will develop less costly routes to the product or cheaper alternative products, effectively causing a loss of investment in the new product. In addition, manufacturers and customers must consider the threat of future regulation changes, which could make the new products obsolete or place them at a competitive disadvantage versus their off-shore competitors.

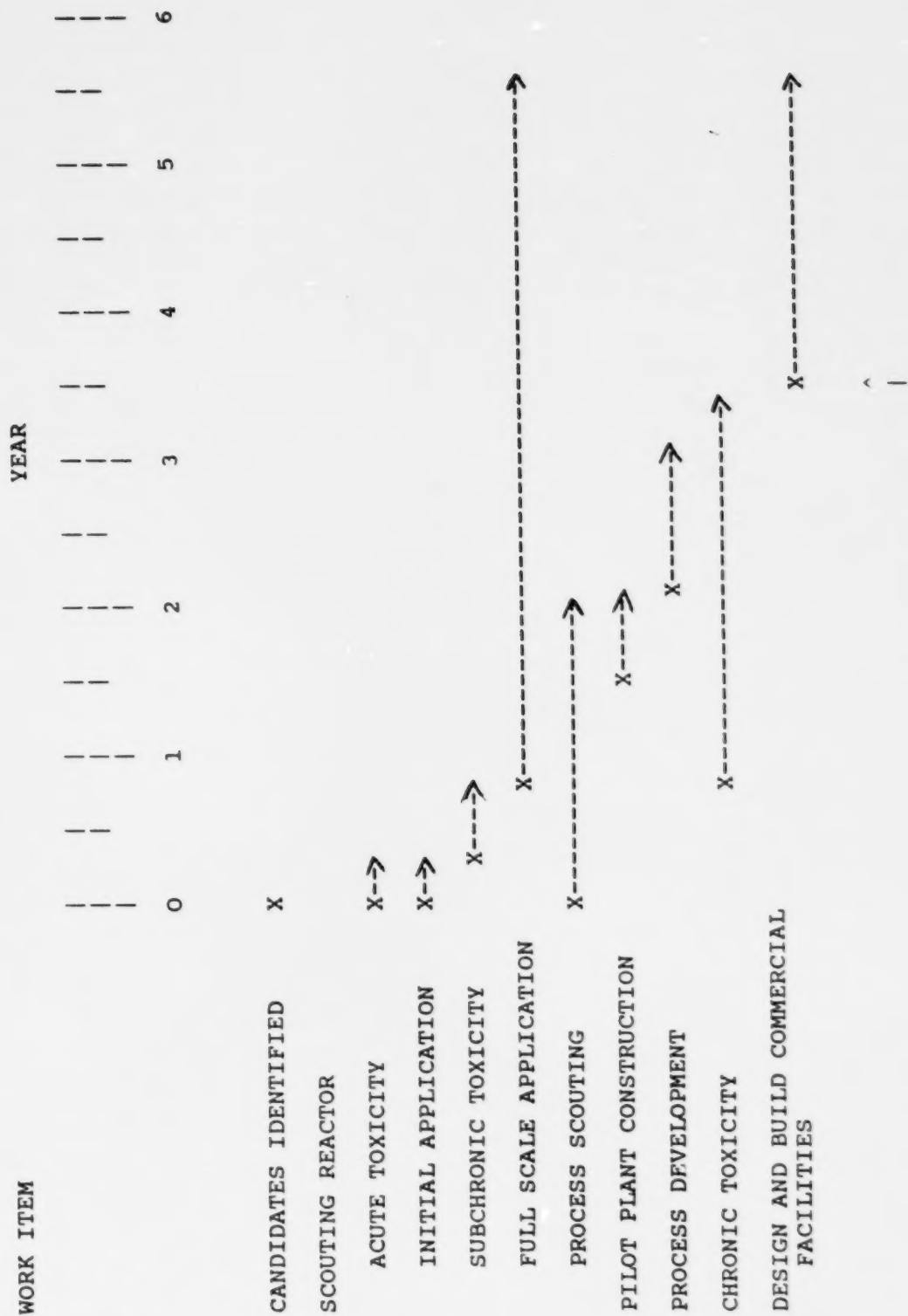
Private sector competition should provide the fastest and lowest cost commercialization of alternatives; however, these conditions must be satisfied if any of the substitutes are to be produced commercially:

- o acceptable cost, toxicity and performance characteristics
- o certainty on ozone and greenhouse regulation
- o marketplace acceptance of substitute cost and performance
- o acceptable return on capital investment, dependent on
 - project investment
 - anticipated sales volume and price
 - product life expectancy adequate to pay off investment

Figure 1 shows a best-case protocol of 5 to 6 years for producing large-scale commercial quantities of CFC substitute products, assuming that unlimited producer resources are available for developing the substitute, customer application testing and redesign are completed within the time required by the producer to build commercial facilities, and no cost, toxicity or market acceptance problems are encountered at any stage of commercialization. A key date is the Go / No Go decision for beginning design and construction of commercial facilities. For this decision to be made between the third and fourth year as indicated, sufficient information must be available on process development, toxicity, and customer applications work. Delays due to problems in any of these areas will delay commercialization.

FIGURE 1

COMMERCIALIZATION PROTOCOL



Significant resources are used to produce adequate quantities of a substitute for toxicity and application testing. Acute toxicity and initial application testing requires 1000 to 10,000 pounds of product at a cost of \$200-300 per pound. Subchronic toxicity and initial customer application testing will use 10,000 to 50,000 pounds of a substitute at \$10-100 per pound. Finally, chronic toxicity tests require 50,000 to 200,000 pounds of product with an estimated cost of \$10-20 per pound.

After testing and economic evaluations indicate commercialization is justified, commercial production facilities must be designed and built, a process that takes two to three years. Plant capacity is based on anticipated sales volume; if too large a facility is provided, the resulting product will bear an inordinate fixed cost burden and might not be provided at a cost affordable to users. The manufacturing process greatly affects the substitute production facility cost and construction time. Investment might be lower if existing facilities could be used or modified. Process conversion of raw materials to finished product determines how much purification equipment is required and what facilities have to be provided for disposal of undesired by-products. Time requirements for processing federal, state or local permits also must be considered in assessing time required to have a facility in production.

Users need sufficient time to evaluate substitute product options, redesign their equipment to handle the substitute and determine how to handle any changes in their product's performance that might result from use of the substitute. For example, Wayne Reedy of Carrier Corporation told the Committee at the April 22 workshop that stationary refrigeration equipment manufacturers would require ten years after receiving initial test quantities of a CFC substitute before they could have all their products using that substitute. Similarly, Norman Nielsen of Chrysler told the Committee that up to thirteen years would be needed to test a substitute and fully convert their production to use that substitute. A new substitute will typically require 3 to 5 years after commercial introduction to significantly penetrate an existing market but may take longer depending on the cost, performance, and availability of the new product versus the same factors for existing products. It should also be noted that products now on the market which use the existing CFCs may become prematurely obsolete if availability of the existing CFCs is restricted.

IID. EPA's Role

The Committee advocated a "three tier" approach for research and commercialization of the substitute products. "Three tiers" refers to three distinct groups of potential CFC alternatives:

- I. "Well known" alternatives previously discussed in May 1986 Radian report, including FC-134a, -123, -124, -141b, 132b
- II. Additional compounds for which substantial information is already available, to be used as fallback position in case unforeseen problems develop with Tier I compounds.
- III. Compounds for which minimal or no information is presently available, to be used as a fallback position from Tier II compounds

Private industry is actively pursuing the research required for the commercialization of the most promising Tier I compounds. To ensure that any new products are environmentally acceptable, the panel advocates EPA funding of these studies to further define potential atmospheric effects (ozone depletion and greenhouse potential) of potential CFC substitutes with highest priority placed on studies of FC-134a and CFC-123:

- o laboratory simulation of atmospheric chemistry
- o computer modeling of atmospheric chemistry

Du Pont feels that the Committee's proposed evaluation of environmental effects of potential substitutes using an atmospheric simulation chamber may encounter problems in accurately simulating atmospheric reaction conditions due to:

- o the number of chemical compounds actually involved in the atmosphere,
- o the variation of atmospheric pressure with altitude,
- o the variation of solar radiation with altitude, and
- o the effects of reactor walls. Surface reactions that would be unimportant in the atmosphere could dominate the chemistry in such a simulation experiment.

Du Pont feels that a more effective approach would be to determine decomposition reaction rate parameters for the substitute compounds in the laboratory and then input this information into existing computer models of the atmosphere.

Panel members disagreed about additional government funding. Some members (including Du Pont) believe that the private sector should pursue all alternatives development while others advocated government funding to build the data base required to assess the commercialization potential of the Tier II and Tier III compounds, including physical properties / synthesis routes, acute toxicity screening, and end-use application screening.

Du Pont feels that EPA can also encourage commercialization of substitutes by:

- o early clarification of ozone depletion and greenhouse regulatory approaches
- o facilitating prompt approvals by necessary regulatory agencies (e.g. pre-manufacturing notices, FDA approvals for food use, etc.)
- o working with CFC users to encourage acceptance of substitutes.

III. FLEXIBLE FOAM BLOWING AGENT CHARACTERISTICS AND CANDIDATES

Table III-1 summarizes boundary characteristics used to screen compounds as potential substitutes for CFC-11 in flexible polyurethane foam applications. Cost requirements for all foam applications are based on cost per mole of blowing agent since equivalent moles of gas would be needed for the foaming application. The best substitute candidates appear to be CFC-123 and CFC-141b; however, a large portion of the flexible foam manufacturers may convert to all water or water/methylene chloride formulations rather than use the higher cost CFC substitutes.

CFC-123 has very desirable physical properties but its cost is projected to be about \$420-840 per kg-mol (\$2.75-5.50 per kg) versus an estimated market limit of \$300-450 per kg-mol. CFC-141b is marginal on meeting the cost requirement with a projected cost of \$250-500 per kg-mol (\$2.20-4.40 per kg) and has the additional disadvantage of being flammable. These barriers will have to be overcome if either of these products is to be a viable substitute for CFC-11 in the flexible polyurethane applications.

Insufficient data exists on most of the remaining candidates (see Appendix B) to adequately evaluate their viability as potential substitutes. This would indicate that these compounds are further away from commercialization than CFC-123 or CFC-141b.

TABLE III-1
FLEXIBLE POLYURETHANE FOAM BOUNDARY CHARACTERISTICS / SUBSTITUTE CANDIDATES

CHARACTERISTIC	PROPERTIES REQUIRED	CFC-11	CFC-123	CFC-141b
Ozone Depletion Potential	Low	1.0	<0.05	<0.05
Greenhouse Potential	Low	0.4	<0.10	<0.10
Normal Boiling Point, °C	25±20	23.8	28.7	32
Gas Efficiency, g	60 min *	Inert	Incomplete	Incomplete
Reactivity with Feed Components	Inert	Inert	Inert	Inert
Solvent Strength in Polyurethane	Low	Low	Low	Low
Flammability	Low	Nonflammable	Nonflammable	Flammable
Toxicity, "TLV" or AEL in ppm **	100 min	1000	100 (AEL)	Incomplete
Heat of Vaporization, kJ/kg	150-350	180	168	223
Miscibility in Feedstock	Complete	Complete	Complete	Complete
Liquid Viscosity, cp at 25 °C	-0.45	0.42	0.45	0.304 at 30 °C
Liquid Density, g/cc at 25 °C	1.25-1.50	1.48	1.475	1.25
Cost, \$/kg-mol ***	300-450 max ****	181	420-840	250-500
(expressed as \$/kg)	2.20-3.30 max (CFC-11)	1.32	2.75-5.50	2.20-4.40

* Original panel report showed 40-60% gas efficiency. A higher gas efficiency is needed to cost-effectively use raw materials.

** "TLV," a registered trademark of the American Conference of Governmental Industrial Hygienists, is the time-weighted average concentration for a normal 8-hour work day, 40-hour work week to which nearly all workers may be repeatedly exposed day after day without adverse affect. AEL, a Du Pont abbreviation for "Acceptable exposure limit," is the exposure limit for chemicals (or for levels of physical agents) set by the Du Pont AEL committee. AELs specify time-weighted average concentrations, doses or biological limits which should not be exceeded and applicable time periods. AEL (8 hour TWA) refers to the exposure limit for a normal 8-hour work day, 40-hour work week.

*** Costs shown for substitutes are derived from Du Pont's March 1987 Fluorocarbon/Ozone Update - values shown reflect estimated bulk pricing in 1987 dollars.

**** Cost exceeding this value may result in customer conversion to all water or water/methylene chloride formulations. Supersoft foam manufacturers may be able to tolerate a higher cost if consumers are willing to pay a premium for soft foams.

IV. RIGID POLYURETHANE FOAM BLOWING AGENT CHARACTERISTICS AND CANDIDATES

Table IV-1 summarizes boundary characteristics used to screen compounds as potential substitutes for CFC-11 in rigid polyurethane foam applications. Cost requirements for all foam applications are based on cost per mole of blowing agent since equivalent moles of gas would be needed for the foaming application. The best candidates appear to be CFC-123 and CFC-141b; however, at their projected market prices, there may be increased use of water formulations by a large portion of rigid polyurethane foam boardstock and systems manufacturers or a switch by insulation consumers to not-in-kind insulating materials. Pour-in-place foam manufacturers should be able to use the substitute products if their cost falls within the lower end of the projected cost ranges.

CFC-123 has very desirable physical properties but its cost is projected to be about \$420-840 per kg-mol (\$2.75-5.50 per kg) versus an estimated boardstock/systems market limit of \$300-450 per kg-mol. CFC-141b is marginal on meeting the boardstock/systems cost requirement with a projected cost of \$250-500 per kg-mol (\$2.20-4.40 per kg) and has the additional disadvantage of being flammable. These barriers will have to be overcome if either of these products is to be a viable substitute for CFC-11 in the rigid polyurethane boardstock/systems applications. CFC-123 or CFC-141b appear to be satisfactory for pour-in-place insulating applications; these applications can tolerate a cost up to \$450-600 per kg-mol since the foam cost has only a small incremental effect on the finished product cost.

Insufficient data exists on most of the remaining candidates (see Appendix B) to adequately evaluate their viability as potential substitutes. This would indicate that these compounds are further away from commercialization than CFC-123 or CFC-141b.

TABLE IV-1
RIGID POLYURETHANE FOAM BOUNDARY CHARACTERISTICS / SUBSTITUTE CANDIDATES

CHARACTERISTIC	PROPERTIES REQUIRED	CFC-11	CFC-123	CFC-141b
Ozone Depletion Potential	Low	1.0	<0.05	<0.05
Greenhouse Potential	Low	0.4	<0.10	<0.10
Normal Boiling Point, °C	25±20	23.8	28.7	32
Gas Efficiency, %	90 min	Incomplete	Incomplete	Incomplete
Reactivity with Feed Components	Inert	Inert	Inert	Inert
Solvent Strength in Polyurethane	Low	Low	Low	Low
Flammability	Low	Nonflammable	Nonflammable	Moderate
Toxicity, "TLV" or AEL in ppm *	100 min	1000	100 (AEL)	Incomplete
Stability	Stable	Stable	Stable	Stable
Quantity for 2 lb/cu ft foam (parts/ 100 parts polyol)	70 max	40-60	45-65	Incomplete
Thermal Conductivity (Btu/hr/ft/F)	0.0055 max	0.0048	0.0054	0.0053
Diffusivity through Polymer	Low	Low	Low	Low
Cost, \$/kg-mol ** (expressed as S/kg) -boardstock and system application	300-450 max 2.20-3.30 max (CFC-11)	181 1.32	420-840 2.75-5.50	250-500 2.20-4.40
-pour-in-place applications	900 max 6.60 max (CFC-11)			

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** Costs shown for substitutes are derived from Du Pont's March 1987 Fluorocarbon/Ozone Update - values shown reflect estimated bulk pricing in 1987 dollars.

V. RIGID POLYSTYRENE FOAM BLOWING AGENT CHARACTERISTICS AND CANDIDATES

Table V-1 summarizes boundary characteristics used to screen compounds as potential substitutes for CFC-12 in rigid polystyrene foam applications. Cost requirements for all foam applications are based on cost per mole of blowing agent since equivalent moles of gas would be needed for the foaming application. CFC-22 was able to meet all of the screening criteria for polystyrene foam sheet applications and is currently commercially available. However, any substitute for this application would have to obtain FDA approval before it can be used for manufacturing containers which contact food. The best other candidates appear to be FC-134a and CFC-142b, but these compounds are at a considerable disadvantage in terms of cost and, for CFC-142b, flammability.

FC-134a meets all of the boardstock screening criteria but it must be brought to market within the low end of its projected \$450-900 per kg-mol (\$4.40-8.80 per kg) price range to satisfy the estimated \$530 per kg-mol market limit. CFC-22 does not meet the criteria for boardstock applications because its moderate diffusivity would result in unacceptably rapid deterioration of insulating performance. CFC-142b is commercially available at a cost of about \$510 per kg-mol (\$5.10 per kg) but its flammability poses workplace safety and liability concerns.

Insufficient data exists on most of the remaining candidates (see Appendix B) to adequately evaluate their viability as potential substitutes. This would indicate that these compounds are further away from commercialization than FC-134a.

TABLE V-1
RIGID POLYSTYRENE FOAM BOUNDARY CHARACTERISTICS / SUBSTITUTE CANDIDATES

CHARACTERISTIC	PROPERTIES REQUIRED	CFC-12	CFC-22	CFC-142b	FC-134a
Ozone Depletion Potential	Low	0.9	0.05	<0.05	<0.05
Greenhouse Potential	Low	1.0	0.08	<0.10	0.08
Normal Boiling Point, °C	-40 to 50	-29.8	-40.8	-9.2	-26.5
Gas Efficiency, %	90 min	>90	Incomplete	Incomplete	Incomplete
Reactivity with Feed Components	Inert	Inert	Inert	Inert	Inert
Solvent Strength in Polystyrene	Low	Low	Low	Low	Low
Flammability	Low	Nonflammable	Nonflammable	Flammable	Nonflammable
Toxicity, "TLV" or AEL in ppm *	250 min	1000	1000	1000	1000 (Provisional)
Stability	Stable	Stable	Stable	Stable	Stable
Quantity for 5 lb/cu ft foam (parts/ 100 parts resin) **	4-6	5-6	3.6-4.3 (est.)	4.2-5.0 (est.)	4.2-5.1 (est.)
Thermal Conductivity (Btu/hr/ft/F)	0.0060 max	0.0056	0.0057	0.0064	0.0048
Diffusivity through Polymer	Not Critical	Low	Moderate **	Incomplete	Incomplete
-foam sheet applications	Low	Low	Moderate **	Incomplete	Incomplete
-boardstock applications	Low	Low	Moderate **	Incomplete	Incomplete
Cost, \$/kg-mol ***	265 max	175	182	510	450-900
(expressed as \$/kg)	2.20 max (CFC-12)	1.45	2.10	5.10	4.40-8.80
-foam sheet applications	530 max				
-boardstock applications	4.40 max (CFC-12)				

* FDA approval is required for any blowing agent used to manufacture polystyrene foam sheet for food containers.
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** Foam density is highly temperature dependent and varies considerably with melt viscosity.

*** Costs shown for substitutes are derived from Du Pont's March 1987 Fluorocarbon/Ozone Update - values shown reflect estimated bulk pricing in 1987 dollars.

VI. REFRIGERATION CHARACTERISTICS AND CANDIDATES

Table VI-1 summarizes boundary characteristics used to screen compounds as potential substitutes for CFC-12 in refrigeration applications. FC-134a was able to meet most of the screening criteria for these applications; however, a new oil will be required if FC-134a is used. Vapor pressure is comparable to that of CFC-12 so users would not have to significantly redesign their systems.

CFC-22 meets the criteria but has a significantly higher vapor pressure than CFC-12 and would require redesign of user systems to handle the higher pressure. Other candidates (including FC-152a and blends with CFC-142b) are commercially available but the presence of flammable components make them of limited interest.

Insufficient data exists on most of the remaining candidates (see Appendix B) to adequately evaluate their viability as potential substitutes. This would indicate that these compounds are further away from commercialization than FC-134a.

TABLE VI-1
REFRIGERATION BOUNDARY CHARACTERISTICS / SUBSTITUTE CANDIDATES

CHARACTERISTIC	PROPERTIES REQUIRED	CFC-12	FC-134a
Ozone Depletion Potential	Low	0.9	0.0
Greenhouse Potential	Low	1.0	0.08
Critical Temperature, C	67 min	112.0	106
Flammability	Low	Nonflammable	Nonflammable
Toxicity, "TLV" or AEL in ppm *	1000 min	1000	1000 (AEL)
Operating Pressures, kPa	3400 max	165	204
Latent Heat of Vaporization, kJ/kg at 0 C	150 min	38	45
Specific Volume of Sat'd Vapor, l/kg at 0 C	75 max		
Fractionation of Mixture Components,			
Temperature Gradient in Evaporator, C	10 max	N/A	N/A
Permeability Through Hose Materials	Not Critical **	Low	Low
Solubility in Current Oils	Complete	Complete	New Oil Req'd
Cost, \$/kg ***	10.00 max	1.45	4.40-8.80

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** Refrigerant does not contact hose in hermetically sealed systems.

*** Costs shown for substitutes are derived from Du Pont's March 1987 Fluorocarbon/Ozone Update - values shown refer to bulk pricing in 1987 dollars.

VII. MOBILE AIR CONDITIONING CHARACTERISTICS AND CANDIDATES

Table VII-1 summarizes boundary characteristics used to screen compounds as potential substitutes for CFC-12 in mobile air conditioning applications. FC-134a was able to meet most of the screening criteria for these applications; however, a new oil will be required if FC-134a is used. Vapor pressure is comparable to that of CFC-12 so users would not have to significantly redesign their systems.

CFC-22 meets the criteria but would require new oil and hoses and its significantly higher vapor pressure would require redesign of user systems. Other candidates (including FC-152a and blends with CFC-142b) are commercially available but the presence of flammable components make them of limited interest.

Insufficient data exists on most of the remaining candidates (see Appendix B) to adequately evaluate their viability as potential substitutes. This would indicate that these compounds are further away from commercialization than FC-134a.

TABLE VII-1
MOBILE A/C BOUNDARY CHARACTERISTICS / SUBSTITUTE CANDIDATES

CHARACTERISTIC	PROPERTIES REQUIRED	FC-12	FC-134a
Ozone Depletion Potential	Low	0.9	<0.05
Greenhouse Potential	Low	1.0	0.08
Critical Temperature, C	93 min	112.0	106
Flammability	Low	Nonflammable	Nonflammable
Toxicity, "TLV" or AEL in ppm *	1000 min	1000	1000 (AEL)
Operating Pressures, kPa	280-1700	280-1700	Incomplete
Latent Heat of Vaporization, kJ/kg at 0 C	150 min	165	204
Specific Volume of Sat'd Vapor, l/kg at 0 C	75 max	38	45
Fractionation (Blends Only), Temperature Gradient in Evaporator, C	10 max	N/A	N/A
Permeability Through Hose Materials	Low	Low	Low
Solubility in Current Oils	Complete	Complete	New Oil Req'd
Compressor Discharge Temperature, C	120 max	94	94
Energy Efficiency, Coefficient of Performance	-2.0	?	?
Cost, \$/kg **	7.50 max	1.45	4.40-8.80

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** Costs shown for substitutes are derived from Du Pont's March 1987 Fluorocarbon/Ozone Update - values shown refer to bulk pricing in 1987 dollars.

VIII. CLEANING AGENT CHARACTERISTICS AND CANDIDATES

Table VIII-1 summarizes boundary characteristics used to screen compounds as potential substitutes for CFC-113 in cleaning agent applications. None of the substitutes was able to meet all of the screening criteria. CFC-132b has some potential for metal cleaning applications but Du Pont has recently disclosed to EPA under TOSCA guidelines that interim sacrifice results from 90-day toxicity testing showed evidence of testicular damage in the test population; final judgement on the viability of this product is reserved until this testing is complete. CFC-123 and CFC-141b have potential to be used in some, but not all, CFC-113 applications. Equipment would likely have to be redesigned to handle these lower-boiling compounds.

Insufficient data exists on most of the remaining candidates (see Appendix B) to adequately evaluate their viability as potential substitutes. Until satisfactory substitute candidates can be identified, conservation measures to control CFC-113 emissions are strongly recommended.

TABLE VIII-1
CLEANING AGENTS BOUNDARY CHARACTERISTICS / SUBSTITUTE CANDIDATES

CHARACTERISTIC	PROPERTIES REQUIRED	FC-113	FC-132b	FC-123	FC-141b
Ozone Depletion Potential	Low	0.8	<0.05	<0.05	<0.05
Greenhouse Potential	Low	0.3-0.8	0.03	<0.10	<0.10
Normal Boiling Point, C	27-75	47.6	46.4	27.6	32
Flammability	Low	Nonflammable	Nonflammable	Nonflammable	Flammable
Toxicity, "TLV" or AEL in ppm *	100 min	1000	5 (AEL) *	100 (AEL)	Incomplete
Chemical Stability	Stable	Stable	Stable	Stable	Stable
Photochemical Reactivity	Low	Low	Incomplete	Incomplete	?
Kauri-Butanol Value	30-100	31	65	61	?
Compatibility with Materials	Non-corrosive	Non-corrosive	Attacks Plastics	Non-corrosive	Non-corrosive
Heat of vaporization, kJ/kg	250 max	147	226	174	223
Vapor Density, g/l at Boiling Point	4.5 min	7.38	5.1	5.8	4.8
Surface Tension, dynes/cm at 20 C	30 max	17.3	16 (at 24 C)	16 (at 24 C)	?
Solubility in Water, Wt %	No Residue	No Residue	No Residue	No Residue	No Residue
Water Solubility in Cleaning Agent, Wt %	Low	0.017 (at 21 C)	0.49 (at 24 C)	0.39 (at 24 C)	?
Cost, \$/kg ***	Low to Moderate	0.009 (at 21 C)	0.085 (at 24 C)	0.083 (at 25 C)	?
	4.00 max	2.20	2.20-4.40	2.75-5.50	2.20-4.40

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** Du Pont verbally notified EPA on May 12, 1987 that interim sacrifice data from a 90-day inhalation toxicity test showed evidence of microscopic testicular damage in the test population.

*** Costs shown for substitutes are derived from Du Pont's March 1987 Fluorocarbon/Ozone Update - values shown reflect estimated bulk pricing in 1987 dollars.

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APPENDIX A

Attendee List for CFC Chemical Substitutes Committee Meetings

Chemical Substitutes Workshop
February 19-21, 1987
Washington, DC

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Chemical Substitutes Workshop

Goals

- o Identify the most promising substitutes for CFCs-11, -12, -113;
- o Estimate cost and time to commercialize these substitutes;
- o Specify necessary market and price preconditions for commercialization;
- o Suggest a communication plan to coordinate research activities with CFC producers and potential users.

Questions

- o What criteria will be used to select substitute chemicals?
- o How much chemical is needed for testing; how much will it cost to produce?
- o What specific factors influence the timing of development and commercialization of these new chemicals?
- o What factors determine market prices of new chemicals?
- o What toxicological testing is necessary? How can it be coordinated with process development and pre-marketing efforts?
- o What are the most innovative research opportunities? (Six CFCs have been targeted by EPA and other researchers: CFC-123, -124, -132b, -133a, -134a, -141b)
- o What are the risks of bring new chemicals to market?
- o What innovative steps can be taken by government to facilitate development and commercialization?

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APPENDIX B

Other CFC Substitute Candidates

Note: Compounds listed in this appendix represent the Committee's initial effort to identify possible CFC substitutes. Subsequent analysis by Committee members has revealed that several of these chemicals are toxic, flammable, or difficult to synthesize. See also Table 4-3 of this report (N.D. Smith).

<u>Chemical</u>	<u>CAS Registry No.</u>	<u>B.P. (°C)</u>
$(\text{CF}_3)_3\text{N}$	432-03-1	- 6
$(\text{CF}_3)_2\text{NC}_2\text{F}_5$	815-28-1	21
$(\text{CF}_3)\text{N}=\text{N}(\text{CF}_3)$	73513-59-4	-31.6
CF_3OCF_3	372-63-4	-59
$\text{C}_2\text{F}_5\text{OC}_2\text{F}_5$	358-21-4	1
$\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_3$	378-11-0	13
CF_2-CF_2 	765-63-9	18
CH_2-O		
CF_2-CF_2 \ O / CF_2-CF_2	773-14-8	0
CF_2-CF_2 	374-12-9	50
CH_2-CH_2		
CF_2-CF_2 	115-25-3	- 5
CF_2-CF_2		
$\text{CF}_2\text{ClCHFC1 (123a)}$	354-23-4	28
CFC1HCFClH (132)	431-06-1	59
CF_2-CF_2 / / CF_2	931-91-9	?

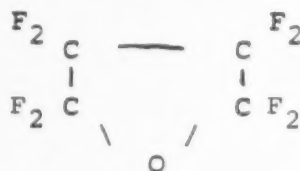
<u>Chemical</u>	<u>CAS Registry No.</u>	<u>B.P. (°C)</u>
$\begin{array}{c} \text{CF}_2\text{-CF}_2 \\ \quad / \\ \text{CH}_2 \end{array}$	3899-71-6	?
$\begin{array}{c} \text{CF}_2\text{-CF}_2 \\ \quad \\ \text{CF}_2\text{-CFCl} \end{array}$	377-41-3	25
C_3F_8	76-19-7	- 38
CF_4	75-73-0	-128
C_2F_6	76-16-4	- 78
$\text{C}_2\text{F}_5\text{H}$	354-33-6	- 48.5
$\text{CF}_3\text{CH}_2\text{F}$ (134a)	811-97-2	- 26.5
CF_3CH_3	420-46-2	- 47.6
$\text{HCF}_2\text{CF}_2\text{H}$	359-35-3	- 20
$\text{H}_2\text{CFCF}_2\text{H}$	430-66-0	5
H_2CFCFH_2	624-72-6	31
CF_3SF_5	373-80-8	- 20
CHF_2SF_5	420-67-7	?
$(\text{SF}_5)_2\text{CF}_2$	1512-21-6	?
$(\text{CF}_3)_2\text{SF}_4$	42179-03-3	?
	42179-02-2	?
	373-74-2	?
$\text{CF}_3\text{CH}_2\text{CHCl}_2$	460-69-5	?
$\text{CF}_3\text{CHClCH}_2\text{Cl}$	338-75-0	?
$\text{CH}_3\text{CCl}_2\text{CF}_3$	7126-01-4	?
CF_3CCl_3 (113a)	354-58-5	
$\text{CHCl}_2\text{CHFCl}$ (122a)	359-28-4	72.5°C
CCl_3CHF_2 (122b)	354-121	73°
$\text{CHCl}_2\text{CHF}_2$ (132a)	471-43-2	60°

<u>Chemical</u>	<u>CAS Registry No.</u>	<u>B.P. (°C)</u>
C_3ClF_5	695-52-3	?
	695-50-1	?
$C_3Cl_2F_4$	22430-77-9	?
	22430-76-7	?
	695-49-8	?
$C_3Cl_4F_2$	6262-50-3	?
$C_3Cl_5F_1$		
$C_3Cl_3F_3$	17371-07-2	
$CHCl_2CF_3$ (123)	306-83-2	27°
CH_2ClCHF_2 (142a)	338-65-8	32°
$CHCl_2CH_2F$ (141b)	430-53-5	?
$(CH_3)_3SiF$	420-56-4	19°
Fluorochlorocyclopropanes		?

Alternatives Categories

- I. Established H-containing haloalkanes
(22, 123, 132b, 134a, 141b, 142b, 152a.
- II. Other H-containing haloalkanes
(122, 123a, 124, 125, 112, 134, 143a.
- III. Halogen propanes
(226, C₃F₈, CF₃CF₂CHF₂, CF₃CHClCF₃, CF₃CH₂CHCl₂, CF₃CHClCH₂Cl).
- IV. Known fluorocarbons and their derivatives

Perfluorofuran



CF₃SF₅
 *CF₃-₅NO
 (CF₃)₃N
 (CF₃)₂SF₄
 CF₂-₂(SF₅)₂
 CF₃N = NCF₃

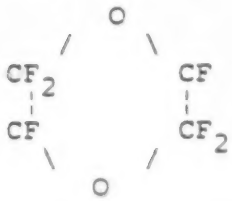
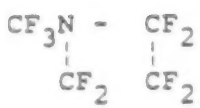
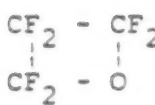
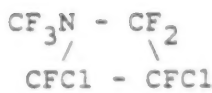
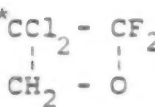
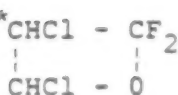


C-318
 H(CF₂)_n H (n = 4 or 5)

- V. Novel Compounds

*Indicates chemicals believed to be toxic (E. Banks, N. Ishikawa, E. Stump)

Additional Alternate CFCs

	bp(C)	Registry #	
CF ₃ CHF CF ₂ Cl	16	359-58-0	
CF ₃ CHClCF ₂	15	431-87-8	
CHF ₂ -CF ₂ -CF ₂ Cl	21	CA 41 P2477b	
CF ₃ CHFCF ₃	17	431-89-0	
*CF ₃ CH ₂ OCH ₂ CF ₃	63	333-36-8	
CF ₃ CH ₂ CF ₃	-1.5	690-39-1	
CF ₃ CHF CHF ₂	?	431-63-0	
CHF ₂ -CF ₂ CHF	-11	680-00-2	
CF ₃ CF ₂ - CH ₂ F			
*CF ₃ O CF ₂ CH ₂ Cl	40		
*CF ₃ O CF ₂ CHFC1	?		
*CF ₃ OCF ₂ CHCl ₂	?		
*CF ₃ OCHF CHCl ₂	?		
*CF ₃ OCFC1 CH ₂ Cl	?		
	23 (18)		9.6
	?		67.5
*CCl ₂ - CF ₂	?		
			
*CHCl - CF ₂	?		
			

	bp(C)	Registry #
* (CF ₃) ₂ NOCF ₃	0.6	
$ \begin{array}{c} \text{CF}_2 - \text{CF}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \quad \text{SF}_4 \\ \diagdown \quad \diagup \\ \text{CF}_2 - \text{CF}_2 \end{array} $	80	
$ \begin{array}{c} \text{CF}_2 \\ \diagup \quad \diagdown \\ \text{CF}_2 \quad \text{N} - \text{CF}_3 \\ \quad \quad \\ \text{CF}_2 \quad \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CF}_2 \end{array} $	47.5	
$ \begin{array}{c} \text{CF}_3\text{N} - \text{O} \\ \quad \diagdown \\ \text{CF}_2 - \text{CF}_2 \end{array} $	-6, 8	
$ \begin{array}{c} \text{CF}_3\text{N} - \text{O} \\ \quad \diagdown \\ \text{CF}_2 - \text{CFCl} \end{array} $	30	
$ \begin{array}{c} \text{CF}_3\text{N} - \text{O} \\ \quad \diagdown \\ \text{CF}_2 - \text{CCl}_2 \end{array} $	63	
$ \begin{array}{c} \text{CF}_3\text{N} - \text{O} \\ \quad \diagdown \\ \text{CF}_2 - \text{CFH} \end{array} $	28	
$ \begin{array}{c} \text{CF}_3\text{CF}_2\text{N} - \text{O} \\ \quad \diagdown \\ \text{CF}_2 - \text{CF}_2 \end{array} $	26	
$ \begin{array}{c} \text{C}_3\text{F}_7\text{N} - \text{O} \\ \quad \diagdown \\ \text{CF}_2 - \text{CF}_2 \end{array} $	50.5	
$ \begin{array}{c} \text{CF}_2\text{Cl} - \text{CF}_2\text{N} - \text{O} \\ \quad \quad \quad \diagdown \\ \quad \quad \text{CF}_2 - \text{CF}_2 \end{array} $	57	and other related $\begin{array}{c} \text{R}_x\text{N} - \text{O} \\ \quad \diagdown \\ \text{CF}_2 - \text{CF}_2 \end{array}$

	bp(C)	Registry #
CH ₂ Cl - CF ₂ CF ₃	27.2	JACS 77, 3149 (1955)
CF ₂ Cl - CFC1 - CF ₃	34.5	JACS 73, 1428 (1951)
CF ₂ Cl - CFC1 - CH ₂ F	56	
CHFCl - CFC1 - CHF ₂	76	
CHCl ₂ - CF ₂ - CF ₃	45	
CF ₂ - CHCl		JACS 83, 382 (1961)
CF ₂ - CH ₂	73	
CF ₂ - CHCl	-40	
CF ₂ - CF ₂		
CF ₂ - O		35818-23-6
O -- CF ₂		
$ \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{CF}_2 \quad \text{CF}_2 \\ \quad \quad / \\ \text{CF}_2 - \text{O} \end{array} $	-10	21297-65-4
CF ₃ OCF ₂ CF ₂ H	?	
CF ₃ OCH ₂ F		2261-01-0
*HCF ₂ OCF ₂ H		1691017-14
CF ₃ CF ₂ OCF ₂ CF ₃	2	Zh org khim 10, 2031, 1974
$ \begin{array}{c} \text{CF}_3 - \text{O} \quad \backslash \quad \text{F} \\ \quad \quad \quad / \\ \text{C} \\ / \quad \backslash \\ \text{CF}_2 - \text{O} \quad \text{CF}_3 \end{array} $	8	Zh org khim 10, 2031, 1974
CF ₃ OCF ₂ CF ₂ OCF ₂ CF ₃	38	Zh org khim
$ \begin{array}{c} \text{CF}_2 \quad \text{O} \quad \text{F} \\ / \quad \backslash \quad / \\ \text{CF}_2 \quad \text{C} \quad \text{OCF}_3 \\ \backslash \quad / \quad \backslash \\ \text{CF}_2 \quad \text{O} \end{array} $	41	Zh org khim

APPENDIX D

SUMMARY REPORT

By:

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Clemson, South Carolina 29634-1905

May 1987

INTRODUCTION

This is a brief summary of my perspective of the deliberations and findings of CFC Chemical Substitute Committee which met for 2.5 days in Washington, D. C. in February 1987 and 2.5 days in Yountville, California in April 1987.

THE PROBLEM

Chlorofluorocarbons (CFC's) have been implicated in stratospheric ozone depletion since 1974 and more recently as climate warming agents. When the hypothesis was first made that long-lived CFC's were reaching the stratosphere where their chlorine was then released by UV radiation resulting in ozone destruction, there was tremendous interest, concern and skepticism. I was personally one of the skeptics, who believed that further research would prove that CFC's were not destroying ozone and that the continued use of these chemicals would pose no environmental problems. I am no longer one of the skeptics and I now believe that the problem is very real. There remains a great deal of uncertainty in the predictions as to the magnitude of the problem but in my opinion, there is a problem.

I have reached this conclusion by examination of many reviews on this subject and by my own inductive and deductive logic. Catalysts can have tremendous effects on chemical reactions even in very low concentrations and it is naive to suppose that hundreds of millions of tons of "inert" chemicals can continue to be emitted into the atmosphere without any adverse effects. It seems that we have to reinvent the wheel periodically; I can recall in my lifetime that lakes and rivers were once viewed as infinite sinks for whatever we chose to dump in them. Of course this turned out to be totally naive and anyone over forty years old can recount a true story of a particular lake or stream that became unfit for most forms of life.

The very reason that CFC's became so pervasive in industrialized society is now the reason they cannot continue to be emitted into the atmosphere in such large amounts. CFC's such as a CFC-11 and CFC-12 are marvelous chemicals. They have ideal chemical and physical properties for so many applications and you simply could not set out today to design and produce more ideal compounds for the applications for which they are so widely used. Unfortunately, their relative lack of chemical reactivity gives them a tremendous lifetime in the atmosphere and essentially all CFC's produced since the 1930's are now in the atmosphere. The most insidious aspect of this fact is that their concentration will continue to rise in the stratosphere affecting the ozone concentration and they will contribute to climate warming or the greenhouse effect for a very long time. The latter may in fact be a much more serious problem with far greater consequences.

In my view, it would be unconscionable to continue the present emissions of fully halogenated CFC's into the atmosphere. Conservation can slow these emissions, but more drastic measures are needed. Unfortunately, any measures to decrease emissions will require international agreement because the atmosphere is dynamic and the problem cannot be addressed on a regional basis.

THE SOLUTION

The obvious solution to fully halogenated CFC's is to stop using them for all but the most essential or critical applications. Like most simple solutions to very complex problems, this is very much easier said than done. These chemicals are essential to present day standards of living in industrialized societies and global development only increases the demand. The next obvious solution is to replace them with "safe" alternatives.

When the CFC Chemical Substitutes Committee was convened, I thought that alternatives would be easy; a little thought soon spoiled this vision. The facts are that the most widely used CFC's, CFC-11, 12 and 113, are nontoxic, noninflammable, have chemical and physical properties which are hard to beat and they are remarkably inexpensive. Almost any reasonable alternative falls short in one of these categories. The most troublesome and difficult requirement, no toxicity, is probably the greatest hurdle for any alternative. Human exposure to present CFC's is both high-level and long-term. Thus, any alternative must be essentially without any toxic effects on man. Very few chemicals, with the requisite physical and chemical properties, low cost and noninflammability, can meet this criterion. The only reasonable alternatives are other fluorochemicals.

It seems clear that any alternatives to present CFC's must have very much shorter lifetimes in the atmosphere and this short lifetime must arise from chemistry in the troposphere, which does not create new menacing problems. The assumption has been made that compounds containing a carbon-hydrogen bond can satisfy this requirement. Very limited data supports the fact that chlorofluorocarbons or fluorocarbons containing a C-H bond are indeed destroyed by attack from OH radicals in a relatively short time. Thus, such compounds would not be significant greenhouse gases and would have very low ozone depletion potentials, relative to presently used CFC's. Much less certain, however, is the ultimate fate of the products from this tropospheric chemistry and whether or not these could pose significant new environmental problems. The educated thinking on this is that such compounds will ultimately rain-out as harmless HX and other innocuous products. In my opinion, this is risk-laden assumption and extensive research will be required to resolve this issue.

In assessing the subject of "safe" alternatives to present CFC's, our committee identified nearly 100 compounds which had the potential, based on chemical and physical properties, to substitute for CFC-11, 12 or 113. Except for previously considered alternatives by industry, toxicity data was non-existent for most of these compounds. Furthermore, most of these alternative compounds have no known industrial process for their production and many were obvious greenhouse candidates with potentially long lifetimes in the atmosphere. It was quite apparent that major industrial producers of CFC's had already identified the most obvious substitutes for CFC-11 and 12 as CFC 123 and 134a, with no "best" candidate for CFC-113, but CFC-132b as a somewhat problematical substitute. In addition, CFC-22, a commercial product, had obvious replacement potential for CFC-12, but not as a plug-in candidate for

refrigeration applications presently utilizing CFC-12. For all of the most promising alternatives excepting CFC-22, toxicology data was incomplete and there exists a real possibility that none of the three alternatives will survive tier III testing. In my opinion, there are no proven alternatives for CFC-11, 12 and 113, except CFC-22 for CFC-12 as noted above.

I do not believe the long-term solution to the environmental problems arising from presently used CFC's can or will be business as usual with alternative CFC's. Any long-term solution must involve substantial global reductions in emissions, regardless of the chemical used. In the short term, certain alternatives can provide some benefits and a major effort must be made to identify these. Long term toxicity data should be obtained for the presently identified best alternatives and their tropospheric chemistry must be exhaustively studied. For other more speculative alternatives, a program should be started to prepare them in sufficient amounts and purity for acute toxicity screening. Those that survive this screen could then be evaluated further in terms of the many variables that must be considered. However, there is little point worrying about an alternative whose toxicity data, even from the most rudimentary screen, is nonexistent.

The implementation of any regulations for presently used CFC's will have to be very carefully considered. Given that there are no proven alternatives to present fully halogenated CFC's other than CFC-22, any regulatory pressure must be able to deal with the potentiality that no other reasonable alternatives will be found. There seems to be a widely held perception that alternatives can and will be found and produced at reasonable costs by the chemical industry. I think this may be possible, but it is by no means a certainty at the present time. The global nature of this problem, the societal and economic implications and the uncertainties that abound, make the ultimate solution of this issue an unprecedented challenge.

APPENDIX E

SUMMARY REPORT

By:

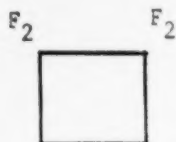
Dr. Nobuo Ishikawa
F&F Research Center
2-9-3 Akasaka
Minato-Ku
Tokyo 107, JAPAN

June 22, 1987

1. Cyclic Fluorocarbons as CFC-Substitutes

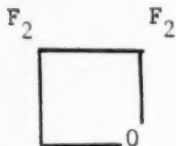
As candidates for CFC-substitutes, some fluorinated compounds which contain hydrogen but not chlorine atoms were suggested at the Washington meeting. Although the following two compounds among them seemed to be the most promising, the data given below make them quite difficult to be considered as candidates.

(1) 1,1,2,2-Tetrafluorocyclobutane



According to a Du Pont's patent, this compound should be prepared by the cycloaddition of tetrafluoroethylene and ethylene under severe conditions ($150^{\circ}C \times 8$ hr), with a low yield (40%). It does not seem to be a practical process for large scale production. Further the boiling point ($60^{\circ}C$) is too high for a working fluid or a foam blowing agent. The high hydrogen content of this compound should make it flammable.

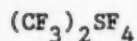
(2) 1,1,2,2-Tetrafluorooxetane



This compound is produced in large scale by Daikin Co., in Japan as a starting material for perfluorinated polyether oil called "Demnum". This oxetane compound is prepared by the cycloaddition of tetrafluoroethylene and formaldehyde, and so it is not costly. The boiling point, $18^{\circ}C$, is also attractive as a working fluid. However, this compound has found to be rather toxic, that is, it is positive to the Ames and mammalian cytogenetic tests. Further it is known to be flammable, flash point being $-16^{\circ}C$. For these reasons this compound also should be excluded from the list of candidates.

2. Sulfur Hexafluoride and Its Derivatives

Trifluoromethylated sulfur fluorides, such as trifluoromethylsulfur pentafluoride and bis(trifluoromethyl)sulfur tetrafluoride, which were also suggested at the Washington meeting, are quite new type compounds as chlorofluorocarbon substitutes as they contain a sulfur atom at the center of the molecule.



There is an interesting investigation on the effect of sulfur hexafluoride on the formation of ozone from oxygen. A few years ago Professor Okazaki and her group of Sofia University in Tokyo published a paper, in which they revealed that the addition of small amount (0.13%) of sulfur hexafluoride to an air ozonizer increased (not decreased) the yield of ozone by as high as 30%.

M. Kogoma, H. Okamura, H. Sugimitu, T. Moriwaki, and S. Okazaki:

SYNTHESE DE L'OZONE PAR L'AZOTE ATOMIQUE DANS L'OZONEUR A AIR

(Journal de chimie physique, 1984, 81, 513-518)

Abstract:

"It is usually assumed that ozone formation in an electric ozonizer results from reactions between electrons and atomic or molecular oxygen, even in the presence of air.

A role of activated or atomic nitrogen can be supposed in an electrical discharge, leading to activated or atomic oxygen which would be the starting compounds for ozone formation. We studied the effects of adding sulfur hexafluoride in small amount, as it can increase catalytically the activated or atomic nitrogen concentration in the discharge. Adding 0.13% sulfur hexafluoride to an air ozonizer increases the yield of ozone by 30%, but induces no change in an ozonizer using pure oxygen. There is therefore one (or several) reactions between molecular oxygen and active nitrogen in the air ozonizer, and this can lead to an increased yield in ozone formation.

This investigation suggests to us that there is a possibility of promotion of ozone formation in the stratosphere if sulfur hexafluoride derivatives are emitted. Of course, under ordinary atmospheric conditions, these compounds should not behave as the catalytic promoter for ozone-formation."

3. Six Chlorofluoroethanes EPA Suggested as Candidates

EPA suggested following six chlorofluoroethanes as probable candidates for CFC substitutes.

CFC-123	CF_3CHCl_2
CFC-124	CF_3CHClF
CFC-132b	$\text{CF}_2\text{ClCH}_2\text{Cl}$
CFC-133a	$\text{CF}_3\text{CH}_2\text{Cl}$
FC-134a	$\text{CF}_3\text{CH}_2\text{F}$
CFC-141b	$\text{CH}_3\text{CFC1}_2$

Among these compounds, FC-134a seems to be the most promising as it contains no chlorine atoms which means that it should have very low ozone depletion potential and also it should be non-toxic. The boiling point (-27°C) is similar to that of CFC-12 (-30°C) and it would be usable as a working-fluid for car air-conditioning. For this purpose, however, FC-134a has too low compatibility with lubrication oil, and it must be an important problem that should be solved in the future.

Production of FC-134a is not too difficult. In general, it is made by the fluorination of CFC-133a, which is not produced in large scale as the intermediate for trifluoroethanol, in Japan.

CFC-133a itself is suggested as one of the candidates by EPA. This compound is produced by the hydrofluorination and fluorination of trichloroethylene with hydrogen fluoride, or by the partial reduction of CFC-123. However, CFC-133a is known to be toxic and it should not be used as CFC-substitute.

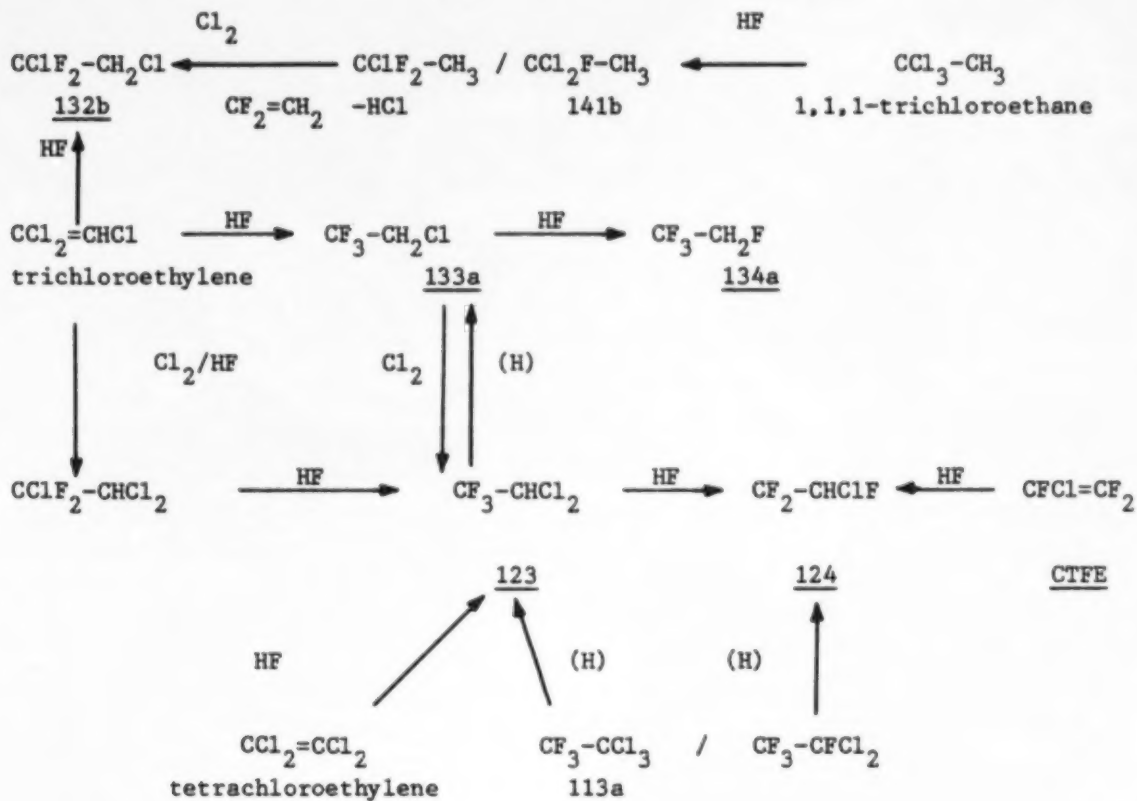
On the other hand, CFC-123 seems to be promising as a substitute for CFC-11 which is now widely used as the foam blowing agent for rigid polyurethane. CFC-123 has a similar boiling point (29°C) to the CFC-11 (24°C). CFC-123 is now produced in Japan in considerable amount by the chlorination and fluorination of trichloroethylene, or by the reduction of CFC-113a (CCl_3CF_3), an isomerization product of CFC-113. CFC-123 is consumed as the starting material for trifluoroacetic acid. Chronic toxicity testing should be carried out as soon as possible.

CFC-132b (47°C) has been expected to be the most probable candidate for the CFC-113 (48°C) substitute. CFC-113 is known as a very useful solvent and is consumed in electronics and other industries in large amounts in Japan. Total production of this solvent has reached about 60,000t in 1986. So it is urgent to find an excellent alternative solvent. However, recent information from DuPont revealed that in their sub-chronic toxicity tests CFC-132b was found to have considerable toxicity. Other compounds which can replace CFC-113 should be investigated. CFC-132b would be prepared by the hydrofluorination and fluorination of trichloroethylene with hydrogen fluoride, or by the addition of chlorine to vinylidene fluoride, which is produced by the fluorination and dehydrochlorination of 1,1,1-trichloroethane.

CFC-124 (b.p. - 12°C) is promising, especially for use instead of CFC-12 as a refrigerant or a foam blowing agent. Various process routes are possible for this compound. Most probable would be the partial fluorination of CFC-123 with hydrogen fluoride, the partial reduction of CFC-114a ($\text{CF}_3\text{CCl}_2\text{F}$), or the addition of hydrogen fluoride to chlorotrifluoroethylene.

CFC-141b is flammable. The use of this compound is, therefore, limited. It could be available by the partial fluorination of 1,1,1-trifluoroethane, but the selectivity for the monofluorination seems to be difficult.

The following chart shows how these substitutes would be produced.



4. The Importance of Conservation

In consideration of the difficulty to find appropriate substitutes for the present chlorofluorocarbons, I have to think again about the importance of conservation, i.e., recovery and reuse of these conventional chlorofluorocarbons. For example, CFC-113, which is widely used as a cleaning agent in various fields as mentioned above, is such an excellent solvent that it cannot be replaced. Even if we could find a comparable solvent, we would have to spend quite large amount of money to carry out, for example, the toxicity tests and to develop a commercial process for manufacturing. The recovery and recycling of CFC-113 is said to be quite difficult because of its high volatility, but it is not impossible. Mechanical improvements of the deep recovery system and physical absorption or concentration of chlorofluorocarbons in the atmosphere are now under development in Japan. When this kind of "high technology" is established, complete conservation would be a much better technique than the use of any alternatives without recycling.

From this point of view, the finding of substitutes for the conventional chlorofluorocarbons should be limited only to those of non-recoverable usage. Propellant might mostly be replaced by alternative gases even though they have some flammability. I think that decomposable fluorocarbon or chlorofluorocarbon substitutes should be used only for special uses. Another non-recoverable case is that of the polyurethane-foaming industry. Some engineers are now trying to find appropriate foaming agents other than chlorofluorocarbons. However, it is said that the soft and cool foaming properties as those of chlorofluorocarbons would not be obtained by any other gases or liquids. In this case new harmless chlorofluorocarbon substitutes should be used as well.

APPENDIX F

SUMMARY REPORT

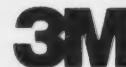
By:

Dr. J. Donald LaZerte
Industrial Chemical Products Division
3M Center
St. Paul, MN

May 4, 1987

Quality Department
Industrial Chemical Products Division/3M
Protective Chemical Products Division/3M

Building 236-1B-10, 3M Center
St. Paul, Minnesota 55144-1000



May 4, 1987

Professor Richard J. Lagow
University of Texas at Austin
Department of Chemistry
Austin, TX 78712

Subject: Summary Report Emphasizing My Concerns and
Recommended Action Points Relating to Substitutes
for Ozone Reducing Chlorofluoro Compounds (CFC's)

1. It is very apparent, from both the open literature and the content of our two committee meetings, that there is a dearth of basic scientific data relating to the behavior of CFC's in the atmosphere. For example, one guest expert told me he knows that CFC's account for the major amount of ozone (O_3) reduction found in the stratosphere. In contrast to the position, a panel member presented data which indicated that present quantities of CFC's released into the atmosphere probably account for very little of the O_3 reduction. Which position is correct?
2. It is very difficult to recommend substitutes for existing CFC's without considering the Greenhouse effect. Because of lack of technical information and the nature of the committees charter, it was necessary to make recommendations considering O_3 reduction only.
3. The committee realized that almost no environmental data existed on the substituted CFC's being recommended. What happens to these new compounds in the stratosphere? Do they degrade to yield trifluoroacetic acid (CF_3CO_2H)? If so, what hazards might this lead to?
4. It is clear that replacing CFC-11, CFC-12 and CFC-113 with new CFC's will take a minimum of five years and a maximum of ten years. If the currently used CFC's are truly responsible for a significant amount of the O_3 reduction, the world cannot continue to release anywhere near the present quantities of these chemicals. Conservation measures should be adopted now. This will require legislation, preferably on a global basis. The author favors an increasing tax levy on CFC-11, CFC-12 and

CFC-113 to provide the incentive to reduce usage and increase recovery. Such measures would also spur the switch to the new CFC's. Moneys collected from the above fees should be allocated to environmental research relating to atmosphere degradation of chemicals.

5. The committee report prepared at the Napa meeting spells out in some detail the position taken relating to the use of CFC-134A, CFC-123 and CFC-132B as substitutes for CFC-12, CFC-11 and CFC-113 respectively. A few points should be added for clarification.
 - a) By far the strongest recommendation relates to the use of CFC-134A ($\text{CF}_3\text{CH}_2\text{F}$ b.p. -26°C) in place of CFC-12 in the areas of air conditioning and refrigeration. It is obvious that several corporations are actively involved in pilot plant and user studies with this material. DuPont's recently issued report (Fluorocarbon/Ozone Update - March 1987) and their announcement at our meeting of projected commercial pricing for CFC-134A indicates that they are very interested in the future business prospects. If the necessary legislation relating to use limits and phase out of CFC-12 is forthcoming, it would appear that at least in the areas of air conditioning and refrigeration a viable substitute is in the offing. However, no corporation will proceed with the very expensive chronic studies unless the market is clearly defined. The statement made by an equipment manufacturer that it would require about six years to test CFC-134A along with candidate compressor lubricants is cause for concern.
 - b) The recommendation relating to the use of CFC-123 ($\text{CF}_3\text{-CCl}_2\text{H}$ b.p. 27°C) in place of CFC-11 is more tenuous. CFC-123 may well be too expensive for use in building insulation products. In addition, its physical properties may be deficient. More applications research with CFC-123 is clearly warranted.
 - c) Recommendations relating to use of CFC-132B ($\text{CF}_2\text{Cl-CH}_2\text{Cl}$ b.p. 47°C) in place of CFC-113 are extremely tenuous. Based on the fact that 132B attacks plastic electronic components, it cannot be used in its present form in this application. Use in the area of metal cleaning would have a somewhat more optimistic future.

- d) Because of the uncertainties expressed in a), b), and c), it is essential that back-up compounds be considered. These are listed in the minutes of the Napa meeting as Tier II compounds. A key compound in Tier II is CF_3SF_5 . It is a possible substitute for CFC-12 should detrimental results develop from continuing work with CFC-134A. CF_3SF_5 could be produced in large volume to meet target economics. At present, virtually nothing is known about its behavior in refrigeration cycles. It certainly would not be a "drop-in product" for use in present equipment. It is recommended that CF_3SF_5 and other Tier II compounds be studied to obtain more property application and environmental data. This will require sponsored governmental research with corporate support to supply the chemicals.
- e) It should be remembered that CFC-22 is an environmentally sound chemical which is presently produced in large volume. Air conditioning and refrigeration manufacturers are reluctant to modify equipment because of the higher pressures and resulting costs. Any incentives for conversion would have benefits.



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APPENDIX G

SUMMARY REPORT

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Houston, Texas

June 19, 1987

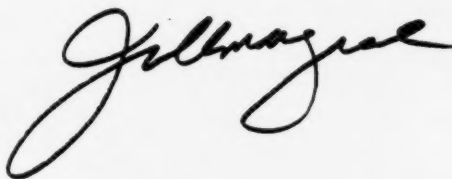
Comments regarding the April 22-24, 1987 Workshop on
Substitute Chemicals for Chlorofluorocarbon Applications

As a result of our three-day review of the known chemistry and anticipated improvements of the chlorofluorocarbon-like materials which could be used in place of Freon-11 and 12 in various air conditioning, refrigeration and foam blowing applications, I would like to indicate my feeling that we made a lot of progress during our meeting. As a result of the discussions, I think everyone has clearly in mind the specific problem involved when chlorine atoms are present in any molecule and the advantages of going to a molecule which has at least one hydrogen available for attack by OH radicals and/or only fluorine as the halogen species present. The questions which were raised are especially significant because of the following points.

1. There is ambiguity in the current state of knowledge regarding the fate of fluorine in the course of upper atmosphere photolysis and ultimate reaction with water or OH radicals. Clearly the fluorine atoms do destroy a small amount of ozone just like chlorine atoms. On the other hand, there is no chain reaction and therefore the effectiveness of fluorine atoms is minimal as contrasted with chlorine (100 as contrasted with 100,000). The ultimate fate of fluorine, however, is quite unclear. HF is certainly one of the major products, but whether there are partially or fully fluorinated forms of acetic acid or possibly other compounds is not currently known.
2. There is an almost total lack of quantitative information about the fundamental properties of the chlorofluorocarbons, the fluorocarbons and the various partially halogenated species which are of special interest to this panel. For instance, there are only a few experimentally determined heats of formation, there is minimal information about bond energies and there is a great need for studies of fragmentation processes both induced by either electron bombardment as in a mass spectrometer (or in the upper atmosphere) or by selected wavelength photolysis (as by a laser or by solar radiation in the upper atmosphere).
3. Although there is a professed interest in funding research by the EPA, it appears that the real efforts are not being funded rapidly. I worry that the time scale which we are talking about for developing an EPA funded research concerned with fluorochlorocarbons, is at least a year or possibly two years away. At the same time, the EPA seems to want assurance from producers that desired compounds that seem to meet the environmental requirements (FC-134a or CFC-123) should be made available in relatively large quantities for user evaluation within two or three years. It would

seem prudent to fund some research immediately which would answer at least some of the major questions and put the selection of particular compounds for evaluation on a firmer footing. Thus, I feel it is crucial that some research programs be initiated immediately for laboratory simulation of the atmospheric chemistry which will be undergone by FC-134a or CFC-123 so that at least the basic questions about the chemistry can be understood with a reasonable degree of confidence.

4. There is a definite need for evaluation of at least 10 or so of the most likely alternative materials which move into the non-traditional areas of chemistry in this field, i.e., the CF_3SF_5 and related subcompounds: the perfluoro-ethers, both linear and cyclic compounds; the chlorofluoro-alkylamines; and probably a few others from the list which was prepared by the panel. Although it may be that the currently suggested materials will solve all the problems, it would be naive to assume that we should not be investigating and obtaining the background data for some of the alternatives. It should be possible to decide whether CF_3SF_5 is really a valid candidate for this kind of usage by a few thermodynamic studies to establish the real stability of this material along with some laboratory simulation of the atmospheric chemistry via matrix isolation spectroscopy or some similar technique. How the sulfur will react with OH, how the compound will be cleaved in the presence of oxygen or hydrogen, whether or not there are significant tendencies to form toxic sulfur-chlorine compounds, etc., can all be deduced rather quickly from a laboratory study. Likewise, the thermal stabilities and likely usefulness of the perfluoroamine derivatives, the perfluoro-ethers, etc., can be concluded from a relatively few simple experiments. We should try to get data of this sort in hand in the next year so that if the problems do not appear to be solved by the current best candidates, then we will have the back-up candidates ready to put into full testing types of situations.



APPENDIX H

SUMMARY REPORT

By:

Dr. Martin A. Robinson
Director
Buffalo Research Laboratory
Allied-Signal, Inc.
Buffalo, New York

May 7, 1987

May 7, 1987

Dr. Richard Lagow
University of Texas
Austin, TX 78712-1167

Subject: Final Report on Deliberation of the EPA Sponsored Panel
for CFC Chemical Substitutes

Dear Dick:

Below is a report on my interpretation of the important points that came out of the deliberations of the Panel for CFC Chemical Substitutes. However, for the record, I would like to restate the Allied-Signal position on chlorofluorocarbons and the environment.

Allied-Signal recognizes that unrestrained growth of CFC's and the related uncertainties as to its atmospheric impact could lead ultimately to unacceptable levels of ozone modification. Therefore, prudent action is warranted.

Since this is a global problem, the US should be actively seeking a global solution through appropriate limitations on growth of CFC productions and CFC emissions. This issue is global in nature, and, as such, unilateral action may impede international resolution.

Development of an intercontinental protocol and its implementation can best be achieved if the protocol is simple in scope and easily implemented. To achieve an international agreement, a simple proposal that focuses on appropriate limitations on the growth rate of CFC 11 and 12 has the greatest chance of success.

Major producing nations (US, ECC) have already indicated their willingness to accept limits on production or production capacity. Negotiations should be continued to reconcile differences.

Allied-Signal continues to conduct research on alternatives that can combine safety with performance. Approximately ten years will be required to fully test, develop and manufacture new alternatives.

Allied-Signal has initiated work with trade associations and customers to develop conservation and recovery programs where applicable.

Dr. Richard Lagow

Additional atmospheric research is necessary and Allied-Signal continues to support, including contributing to the funding of, such research.

As new information becomes available, Allied-Signal will review the situation and alter its position as appropriate.

Let us now turn our attention to the actual deliberations that occurred at the two meetings of the panel, and, my interpretation of the salient points that emanated from these discussions. A most important factor is that government regulations will force change. However, these regulations must be reasonable or they will be counterproductive. The impetus resulting from regulations, will certainly induce several companies to consider producing materials which, currently, appear to be acceptable replacements. There are, however, certain obstacles that bear mentioning. The time element is probably between six and nine years for a company to fully commercialize a replacement CFC. A major part of this timing is the third tier toxicity testing which can take anywhere from two to five years for total approval. Certainly there are short cuts but it is questionable whether the chemical companies would take a chance on compromising the accepted testing regimen. Also, a very dark cloud looms overhead, which is called the greenhouse effect. Because of the large investment necessary to commercialize new replacement materials, companies will be a bit hesitant about making large investments to obviate the ozone problem only to find out that they are now contributing to a new problem. Particularly cogent to this line of reasoning is the uncertainty regarding tropospheric decomposition of CFC-134a. Neither the experts (including S. Roland) nor the panel members appears to be able to definitively describe the decomposition mode or resulting products. If one assumes that CFC-134a totally decomposes to give HF then this effect will be quite different from that if the hydrolysis product is trifluoro- or monfluoroacetic acid. Therefore, in summary, companies are being asked to commercialize replacement materials without knowing fully their contributions to the greenhouse effect, acid rain effect, or the other problems that may arise somewhat further down the road. Since the investment is quite large, companies certainly will have to equate risk against return.

It was obvious that a consensus existed within the Panel relative to the materials to be used as replacements in the major CFC applications. These include the following:

Dr. Richard Lagow

For autos - 134a; some large air conditioning units of the stationary variety - 22; for solvent applications there appears to be no universal replacement but a significant amount of 113 can be conserved by altering the configurations of the most common equipment and there are some possible replacements for various aggressive solvent applications such as 132b; finally, in the blowing agent area, the applications are quite diverse and 123 is probably the best current replacement but at the expense of increased price and decreased efficiency.

With regard to the time necessary for full commercialization of candidate materials, it would appear that six to nine years will be required. It is more likely that the longer period of time will be necessary because of both third tier toxicity testing and the fact that there may have to be some significant modifications in existing plants or the need to build entirely new plants. Further, a point not discussed in detail, has to do with the increasingly complex waste disposal problems. For the production of many of these replacement materials, catalysts are required which have to be handled under controlled conditions. With the increasing difficulty for the removal and disposal of these materials, this can emerge as a very significant problem.

It was quite apparent from the discussions that a unconventionally different chemical to replace the chlorofluorocarbons was not at hand. Materials which were mentioned such as SF_5CF_3 or cyclic heteropoly molecules have apparently not been studied for this application in any significant detail. Therefore, the idea of EPA sponsored programs for the development of new, longer range products as CFC replacements is one that should be seriously considered. Along these lines a second obvious area in which programs should be supported is in the study of tropospheric chemistry relative to the replacement candidates. It is very important to know their fate under tropospheric conditions whether by hydrolysis or light decomposition. This could most quickly be evaluated in a laboratory specifically set up for this purpose and, the EPA could facilitate this activity. Finally, at the fear of being pompous, I would suggest a committee composed of representatives from government, industry and academia be set up so that they can chart the direction of these programs particularly the latter. It is very important that the studies be conducted on the proper materials and the data be translated into meaningful results as quickly as possible so that any impact on commercialization can be taken into account.

Dr. Richard Lagow

A point that has to be reemphasized is that the ozone problem is not an island unto itself. In attempting to solve the ozone problem, one is, perhaps, introducing potentially greater problems in terms of the greenhouse effect and acid rain. Consequently, the risk is rather great for the participants that seek to play the game because, in solving the ozone problem, there is uncertainty with regard to new problems that could arise.

Finally, in terms of a summary, I would like to direct myself, succinctly, to the answering of John Hoffman's questions as outlined in his letter to R. Lagow which preceded the second panel meeting.

1. What is necessary for chemical alternatives to compete with current CFC's?

Chemical alternatives first and foremost must be viable in their application in terms of performance but do not necessarily have to directly compete in cost with existing materials. Of course, the more cost competitive the replacements are, the less likely that searches for cheaper alternatives will be undertaken. However, in an application such as automobile air conditioners, increased cost can and will be sustained. In other areas (i.e. blowing agents) a performance/cost relationship which, if it is not fairly close to that of existing materials, will be more difficult to accept. Therefore, competition relative to price will be sensitive to the area of application.

As to reducing costs for testing, production, etc., that is the direct responsibility of the commercializing company. Prudent risks might be acceptable but there are limits. No company would want to be irresponsible under any circumstances. However, any shortcuts to be taken would be entirely the purview of the respective company since they retain the ultimate liability.

2. Will production of CFC-123 and CFC-134a be limited to one production process by one company or will several companies be capable of offering these products?

It is rather unreasonable to believe that the above mentioned CFC's will be limited to one company. More likely, several companies will be producers by several processes or, at least initially, by major variations of one common process.

Dr. Richard Lagow

3. What is the importance of producing chemicals for testing by users and when should these test quantities be made available?

The ultimate test for any potential product is user acceptance. Therefore, testing by potential users should be initiated as early as the producing company feels is possible with the supply of requisite amounts of materials probably being the limiting factor. The successful development of a product usually involves an interplay between the producer and user with fine tuning occurring along the way to commercialization.

4. When should toxicity testing begin and should it be jointly conducted by businesses and government to save time and resources?

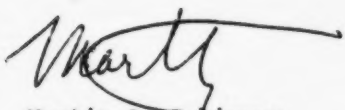
There are three tiers to toxicity testing. The first two are relatively cheap and, for the most part, undertaken early in the development curve by the individual company. A situation, such as the CFC replacements, is rather unusual because several companies are simultaneously thrust into development of, presumably, the same materials. Consequently, this offers the opportunity of the sharing of Tier III toxicity costs. Since the ultimate liability lies with the producing company, I doubt that they would accept anything short of direct participation and control. Thus, government testing would not be of value; government subsidy may be acceptable; joint testing by several interested companies could probably be arranged.

5. What are the necessary financial conditions to speed product development, testing and commercialization?

A decision to compete in the product arena would presumably be made on computed financial considerations, taking into account the risk/reward ratio, etc. External subsidy is probably not applicable in the CFC area. Prudent compromise on data accumulation is a possible mode of acceleration. Competition, relative to market arrival is another. However, the schedule of commercialization distributed at the meeting by du Pont demonstrates that, at the most, a year can be shaved from the time schedule.

Dr. Richard Lagow

From my perspective the meeting was a very productive one. It brought together industry, academia and government in an honest attempt to discuss a very pressing problem. If we proceed in a rational and consistent manner, I am sure that the problem of ozone depletion will be successfully controlled.

A handwritten signature in cursive script, appearing to read "Marty", with a long horizontal flourish extending to the right.

Martin A. Robinson
Director
Buffalo Research Laboratory

MAR/mc

APPENDIX I

SUMMARY REPORT

By:

Professor Dr. Herbert W. Roesky
Anorganisch-Chemisches Institut
Universitat Gottingen
Gottingen, Federal Republic of Germany

May 11, 1987

R e p o r t

Chlorofluorocarbons have a broad application. The outstanding characteristic properties are low toxicity, nonflammability, moderate solubility and heat transfer characteristics. All of these factors must be considered along with potential environmental and economical impacts in choosing substitutes. We have to deal with a whole package of problems.

Alternative chemicals which do not deplete the stratospheric ozone are only one possibility to solve this problem. We have to be aware that the new chemicals which substantially degrade in the troposphere might cause long term problems with increasing amounts of toxic decomposition products. Under optimistic conditions and extensive tests these chemicals might be introduced to the market not before 1993.

Alternative recommendations to avoid the depletion of the ozone layer and the increasing green-house effect might be the following :

1. Before new products are available, blends of CFC-11 or CFC-12 with CFC-22 could be used, which will reduce considerably the ozone depletion and the green-house effect. The life time of CFC-22 in the troposphere should be substantially shorter compared to CFC-11 and CFC-12 and this will result in a smaller green-house effect. Many other mixtures are possible and useful.

2. Recycling of the known chlorofluorocarbons is another possibility instead of using new chemicals. The manufacturers of air-conditioners and refrigerators should guarantee no leakage of the apparatus within ten years of operation. A sealed system should be used. Maintenance of the cooling system should not be necessary. For this purpose only other fittings and hoses are necessary. CFC-22 should be used preferentially for refrigerators, it is still one of the best alternatives to CFC-12.
3. The compounds mentioned in the list which contain more than four halogens, will generate on hydrolysis additional acid rain in comparison to CFC-11 and CFC-12. Of course this amount is relatively small compared to other sources of the acid rain, but a long term increase of HF as an aerosol might cause some health problems.
4. It has been reported that the concentration of CFC-113 in the troposphere is increasing gradually. This compound is an important solvent in the electronic and dry cleaning industry and, therefore, should be handled in closed systems in the future.
5. Conservation of the current chemicals CFC-11, CFC-12, and CFC-113 can be reached if regulations increase their price substantially.

APPENDIX J

SUMMARY REPORT

By:

Andrew J. Woytek
Research Director
Air Products and Chemicals, Inc.
Allentown, PA

May 21, 1987

CHLOROFLUOROCARBON CHEMICAL SUBSTITUTES REPORT

Andrew J. Woytek
Air Products and Chemicals, Inc.
Allentown, PA 18103

INTRODUCTION

My participation in the Committee on Chlorofluorocarbon Chemical Substitutes primarily focused on the issue of economics and commercialization of potentially new products. Therefore, my report deals with these issues as they relate to the potential processes and economics for various new products. Also, in my current position with Air Products and Chemicals, I have association with the electronics industry and knowledge of the use of their chemical products and will comment on the use of solvents in the electronics industry.

ECONOMICS

Since potential substitutes for the current CFC's are likely to be fluorine containing compounds, an understanding of the various economics for producing fluorine compounds is necessary. There are three basic methods for producing fluorine compounds, e.g.

1. Exchange reactions with chlorocarbons through Swarts reaction chemistry utilizing hydrogen fluoride such as is currently practiced for the production of the commercial chlorofluorocarbons.
2. Electrochemical fluorination in anhydrous hydrogen fluoride to produce perfluorinated amines, acids, ethers, etc.
3. Indirect or direct fluorination using elemental fluorine to produce perfluorinated fluorocarbons.

Attached in Table I is a summary of various selling prices for commercial products made through these technologies. The table shows typical products made by these various processes and the maximum value which can be attributed to the fluorine content of the product based on all of the cost assigned to fluorine. This can be analyzed as the maximum value of the fluorine contained in each of these individual molecules.

In addition, Table I shows the value of fluorine as it is found in its natural occurring state as fluorspar, calcium fluoride. In this case, the value of the fluorine is 19¢/lb as sold in the mineral. Table I also shows the increased value of the fluorine as it is converted into HF by the common sulfuric acid processes to produce hydrofluoric acid. The fluorine value increases to 73¢/lb as it is currently sold as hydrofluoric acid. Both these materials are considered commodity products with over 400 M^a tons of hydrofluoric acid consumed in the United States with approximately 50% used in the manufacture of CFCs.

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Table I shows four of the common commercial chlorofluorocarbons with their corresponding selling prices and the value of fluorine in the molecule. The value of fluorine for these products varies from ~\$2-4/lb. If CFC-11 is eliminated from the analysis, since it contains a very low percentage of fluorine, the remaining products vary between \$2.14 to \$2.90/lb. Therefore, a value of \$2-3/lb of contained fluorine in a product produced by Swarts chemistry utilizing HF can be anticipated. Based on these analyses and utilizing \$2.90/lb, which is the value of fluorine in CFC-113, a projection of the selling prices of the proposed C₂ chlorofluorocarbons can be made. CFC-123, which contains 46% fluorine, would project to \$1.33/lb. For CFC-134a, which contains 75% fluorine, the projected selling price would be \$2.18/lb.

There are many factors which effect the selling price of chemicals, including investment, raw material costs, yields, and volume of production. This analysis for the projected cost of new chemicals would give a reasonable ballpark estimate, assuming similar technologies currently used for the production of CFC-113 are used in the production of the newer chemicals, CFC-123 and 134A.

Table I also shows a group of chemicals including sulfur hexafluoride (SF₆), carbon tetrafluoride (CF₄), and perfluorperhydro-phenanthrene (C₁₄F₂₄) which are made either directly or indirectly through elemental fluorine. These products are representative of commercial chemicals which are currently produced in volumes of 1-10 MM lbs/year. These quantities are far less than the production volumes of chlorofluorocarbons which run into the hundreds of millions pounds per year.

SF₆ is the largest volume producer, being estimated at 10-15 MM lbs/year worldwide and represents the largest merchant product sold based on elemental fluorine. This excludes production of uranium hexafluoride (UF₆) which is done either captively or on a toll basis. Some producers, such as Allied, combine SF₆ and UF₆ production to effect economies of scale. In analyzing product cost based on elemental fluorine, SF₆ gives the most favorable number with the value of contained fluorine based on current selling prices to be \$4.50/lb. Therefore, any process which utilizes elemental fluorine as a raw material could be anticipated to have this selling price value for the fluorine contained in the molecule. This could be reduced somewhat with larger scale plants if production volumes for products based on elemental fluorine were in the same hundreds of millions of pounds which are currently used for the production for chlorofluorocarbons.

Carbon tetrafluoride is another product which is analyzed in Table I. This product is produced commercially by technologies either utilizing HF or fluorine, and is priced competitively by both processes. The value of fluorine in CF₄ is considerably greater than that in SF₆ (\$11.60/lb versus \$4.48/lb). However, CF₄ is produced in significantly smaller quantities than SF₆ and has critical purity requirements in its major use in the electronics industry which has a significant impact on production costs. Also, when dealing with fluorination of hydrocarbons with elemental fluorine, only half the fluorine ends up on the molecule with the other half going to hydrogen fluoride. Therefore, the theoretical amount of fluorine required is

approximately twice that which is contained in the final product. Although the HF can be recovered in the process, its value is far less compared to the value of the fluorine as it is used in a raw material in the process.

Table I also shows the economics for a more complicated perfluorinated cyclic material, namely, perfluoro-perhydro phenanthrene. This material is typically produced through indirect fluorination reactions such as cobalt trifluoride with fluorine being the consumable chemical. In this case the value of the fluorine in the molecule is ~ \$49/lb. However, it should be borne in mind that this is a very complex chemical with yields and efficiency of the process having a significant impact upon the final cost. Again, the theoretical requirement for fluorine is approximately twice that contained in the final product.

The third category shown in Table I are two typical products which are made by electrochemical fluorination. These are perfluoro tributylamine and perfluoro tripentylamine. The value of fluorine in these molecules varies from \$32.77/lb in the butyl compound to \$49.80/lb in the pentyl compound. These products are commercial materials produced in volumes of < 1MM lbs/year and thus far less than the volumes of current chlorofluorocarbons. Therefore, there could be a significant impact of volume on the price of these specialty products with significant reductions with increasing volumes. Since these materials are complex molecules, yield plays a significant factor in determining the final selling price of the chemical. For simpler molecules (less number of carbons), it would be anticipated that selling prices could be considerably less.

In the fluorination of organic molecules by the electrochemical process, equivalent electrical energy to the process using elemental F_2 is required. Since only half the equivalent electrical energy appears as fluorine on the molecule with the other half being used to generate HF by-product, economics based on investment and operating cost would be similar to processes utilizing fluorine.

In summary, it is projected that Swarts type chemistry utilizing HF would yield the most cost efficiency process for producing new fluorocarbons at approximately \$2 to \$3/lb of contained fluorine. Electrofluorination and direct fluorination would be more costly, with a contained fluorine value of a minimum of \$4.50, based on current market data. This technology could offer an economic advantage for perfluorinated compounds where yields and efficiency of the Swarts type chemistry results in higher processing costs.

Another issue which must be considered in the manufacture of alternate fluorocarbons is the availability of hydrofluoric acid, the key raw material. Because of the large volume of new chemicals required (>1,000 MT), new chemicals would have to be produced by companies which are basic in hydrofluoric acid or have access to a source. Table II is a list of companies worldwide having HF capacity and the producers would likely come from this list.

PILOT PLANT MANUFACTURE - F₂ BASED PRODUCTS

The issue of producing sufficient test quantities of new materials to conduct Tier One toxicity testing and initial functional application testing was discussed at length during the meetings. It was generally agreed that up to 10 M lbs of material would be required at this level. My comments will be restricted to producing these quantities of products utilizing elemental fluorines based on my Company's raw material and technology position in this area.

A company such as Air Products which has fluorine production capability and technology for the production of fluorocarbons could be in a position to rapidly produce significant quantities of fluorocarbon for testing if the chemistry was known. I would anticipate only a short development program in the laboratory lasting less than three months. Assuming current processing equipment could be used with little modification, I project that the process could be operated in the pilot plant with the production of 10-20 M lbs completed within one year. If the pilot plant production equipment were not available and it involved new process technology, I would envision a 6-9 month additional timeframe to design and install the necessary equipment.

The following is an estimate of the time and cost for various scenarios to produce quantities of product depending upon the knowledge of the process and the equipment availability.

- Known Process--Equipment Available (\$1-\$3 MM)

Laboratory Synthesis	1-3 Months
Production	6-9 Months
First Substantial Product Available	6 Months

- Known Process--Pilot Equipment Not Available (\$2-\$5 MM)

Laboratory Synthesis	1-3 Months
Design/Construction	9-12 Months
Production	9 Months
First Substantial Product Available	15 Months

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• New Process--Pilot Equipment Not Available (\$2.5 - \$5.5 MM)

Laboratory Synthesis	6 Month Minimum
Design/Construction	12 Months
Production	9 Months
First Substantial Product Available	21 Months

A known process would utilize existing technology such as direct fluorination with fluorine or indirect fluorination utilizing cobalt trifluoride and also assumes that the feedstock hydrocarbon is available. A new process would be for a chemical which has not been previously reported in the literature as being produced by commercial technologies or utilizing an entirely new fluorination method. This case would also pertain to a product utilizing a feedstock which is not commercially available.

The estimated cost for the various scenarios presented above would be in the several million dollar range. For the first case, a cost of \$1,000,000 to \$3,000,000 would be projected. For the second scenario an additional \$1,000,000 to \$2,000,000 to cover the investment cost of new equipment would be required. For the third scenario an additional half a million dollars to cover laboratory development costs would be required and it is likely that the investment in the plant would be in the \$2,000,000 range. The amount of product produced in the pilot plant would be dependent upon yields and the efficiency of the process. I would estimate a minimum capability for producing approximately 1,000 pounds per month during the campaign to produce the given product.

FOAM BLOWING--CHEMICAL COSTS

An analysis of the cost of the currently used CFC-11 and CFC-12 on a volume basis (per cubic foot) and some alternates to be considered is presented in Table III. Also, a comparison of the thermal conductivity of various materials for evaluation as thermal insulation is contained in the table.

The table shows that on a volume basis CFC-11 and CFC-12 cost approximately \$22 per hundred standard cubic foot. This represents a significant portion of the cost of foam--15% to 30%. CFC-123 at a selling price of \$2.50/pound with comparable thermal conductivity will cost \$108 per hundred standard cubic foot. Several other commercially available perfluorinated materials such as SF₆ and CF₄ were also analyzed. These materials do not have thermal conductivities as low as the CFC's and would be priced in excess of \$100 per hundred standard cubic foot.

Also shown in the table is a cost analysis for atmospheric gases and their cost and thermal conductivity. As can be seen, there would be a significant reduction in cost if gas blowing could be accomplished with materials such as

CHLOROFLUOROCARBON CHEMICAL SUBSTITUTES REPORT
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nitrogen, argon, or CO₂. The thermal conductivities of argon and CO₂ are comparable and approximately double that of the chlorofluorocarbons. Therefore, twice the thickness would be required for equivalent insulating properties. With the economic incentives that could be achieved with using more environmentally acceptable gases such as argon and CO₂, a technology program to develop gas blowing technology for foams would be justified since the use of CFC-123 at current projected prices does not appear to be a feasible economic solution. Alternates to CFC-123 using cheaper materials must be investigated.

ELECTRONIC APPLICATIONS--CFC-113

Based on my discussions with various users in the electronics industry CFC-113 has found wide spread use as a solvent in many applications. It is used as a general purpose solvent in the clean room area to big volume continuous machines for cleaning printed circuit boards. These continuous conveyorized machines appear to be a large user of solvent with significant losses through the exhaust system and carry out with the printed circuit board components. There appears to be little incentive for controlling the loss of this solvent during use since it is relatively inexpensive--less than \$1/pound. In a typical application, high volume of the hot solvent is sprayed on the printed circuit board which leads to large losses of the material through vent systems and carry out on the board. I believe a significant reduction in usage would occur with a increased selling price for Freon-113 which would drive both the machine manufacturers and the electronic consumers to conserve on the usage of this material.

The Semiconductor Industry Association (SIA) has formed a Task Force to review the usage and application of CFC solvents in the industry. I have been in touch with the Chairman of the Task Force and recommend that the EPA maintain a contact with this committee. The chairman of the Task Force is Court Skinner of National Semiconductor located in Santa Clara, California.

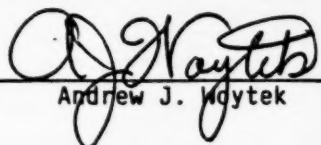
ADDITIONAL ISSUES

The following are my impressions and recommendations on general issues which were raised during the course of the meeting:

1. The fate of trifluoroacetic acid which is proposed as a degradation product from the proposed CFC-123 and CFC-134A must be studied in further detail. The impact of the significant quantities of this material which will be rained out on the earth's surface should be studied and understood. Although the quantity of this material will be small, relative to the amount of currently generated acid rain, it is a new chemical which could have a significant environmental impact.
2. The general fate of perfluorinated fluorochemicals was not totally addressed at the meeting. Although it appeared to be generally accepted that perfluorinated chemicals are acceptable and Sherry Rowland indicated in his talk there was no decomposition of CF₄, a general statement on

their safety was not issued as part of the findings of the committee. Many of the substitute chemicals that were identified were perfluorinated materials. Therefore, I would recommend that a general statement be made that perfluorinated fluorocarbons are considered to be totally safe substitutes.

3. The committee identified a number of potential new chemicals as long range substitutes. I recommend that this list of chemicals be further screened and a more manageable list be identified with corresponding applications. A strong recommendation from the committee on either one or two potential long range substitutes for each of these applications would stimulate more research on these specific compounds.
4. After screening of the list of potential new compounds, I would recommend that funding by the EPA be furnished to academic and research organizations where there is a lack of synthesis or physical property data on these materials. This will answer the question as to whether a specific compound is viable from both the synthesis and economic standpoint as well as its chemical and physical properties.
5. Funding should be provided to develop a laboratory model to understand the ultimate degradation of any of these products which are released to the atmosphere. This is certainly not an easy problem but is required to gain confidence as to the ultimate fate of any new compounds being introduced into the atmosphere.


Andrew J. Woytek

AJW/bb
2103g

- a) $M = 10^3$
- b) $MM = 10^6$

TABLE I
FLUORO-CHEMICAL ECONOMICS
SELLING PRICES

	<u>Process</u>	<u>\$/LB.</u>	<u>- Fluorine -</u>	
*			<u>%</u>	<u>\$/LB.</u>
CaF	Mineral	0.09	47	0.19
HF	H ₂ SO ₄ Process	0.69	95	0.73
CFC13 (FC-11)	HF	0.57	14	4.16
CF ₂ Cl ₂ (FC-12)	HF	0.68	32	2.14
CF ₃ -CCl ₃ (FC-113)	HF	0.89	31	2.90
CHCl F ₂ (FC-22)	HF	1.05	44	2.37
SF ₆	F ₂	3.50	78	4.48
CF ₄	HF/F ₂	10.00	86	11.60
Cl ₄ F ₂₄	CoF ₃ /F ₂	36.00	73	49.20
(C ₄ F ₉) ₃ N	EC	25.00	76	32.70
(C ₅ F ₁₁) ₃ N	EC	38.00	76	49.80

* 1987 Published Selling Prices

TABLE II
WORLD PRODUCERS OF HYDROFLUORIC ACID

	CAPACITY (<u>THOUSANDS OF SHORT TONS</u>)
UNITED STATES (2)	
ALLIED-SIGNAL	95
E. I. DUPONT DE NEMOURS	75
PENNWALT CORP.	26
ESSEX CHEMICAL	<u>10</u>
SUBTOTAL	206
EUROPE	
ATOCHEM	44
BAYER	50
KALI-CHEMI	28
MONTEFLUOS	33
ICI	55
ISC	13
RHONE POULENC	9
AKZO CHEMIE	9
OTHER	<u>127</u> (1)
SUBTOTAL	360

TABLE II
WORLD PRODUCERS OF HYDROFLUORIC ACID
 (CONTINUED)

	CAPACITY <u>(THOUSANDS OF SHORT TONS)</u>
JAPAN	
ASAHI	20
DAIKIN	15
HASHIMOTO CHEMICAL	55 (1)
OTHERS	<u>35 (1)</u>
SUBTOTAL	125
MEXICO (PRIMARILY FOR EXPORT TO U.S.)	<u>123 (1)</u>
TOTAL	814

(1) NO SIGNIFICANT CFC'S PRODUCED.

(2) DOES NOT INCLUDE HF FOR CAPTIVE CONSUMPTION BY ALUMINUM
 METAL PRODUCERS

SOURCE--1986 CHEMICAL ECONOMICS HANDBOOK

TABLE III
FOAM BLOWING

<u>Gas</u>	<u>Btu/Hr • Ft • °F</u>	<u>\$/100 Ft³</u> *
CFC-11	0.00489	22.00
CFC-12	0.00557	21.60
SF6	0.00813	140.00
Ar	0.0103	2.35
CO2	0.0100	0.34
N2	0.0150	0.43
Air	0.0124	-
CFC-123	0.0054	108.00
CF4	0.0095	
" (@\$5.00/lb)		123.00
" (@\$10.00/lb)		246.00

* 1987 Published Selling Price

2105g/2

APPENDIX K

SUMMARY REPORT

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April 22, 1987

SOME COMMENTS ON CFC SUBSTITUTES

1. Introduction

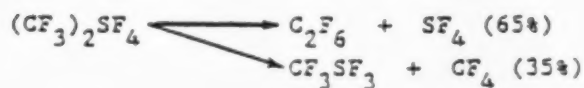
I understand the global concern about environmental problems based on the probable ozone depletion in the stratosphere induced by some CFCs.

The existing CFCs, however, must be the best compounds from the view points of their cost, performance for each application and safety except too much stability in the troposphere, and it is extremely difficult to determine the CFC substitutes which will satisfy all the requirements.

Therefore, the reduction of consumption of CFCs by mixing with those compounds having less ozone depleting potential and the effective recycling system for CFCs should be considered in the first step.

2. Environmental consideration

Most of CFC substitutes except perfluorinated compounds may generate hydrogen fluoride by the possible decomposition reaction in the troposphere. The sulfur-containing CFC substitutes we discussed in the Washington meeting, were reported to decompose thermally to generate highly toxic sulfur tetrafluoride as follows:



Sulfur tetrafluoride is subjected to hydrolysis to generate hydrogen fluoride and sulfur dioxide. If these decomposition would take place photochemically in the troposphere, these compounds may be excluded from the list of potential candidates.

There seems to be some doubt of the accumulation of R-113 in the stratosphere, although the concentration of R-113 in the troposphere has been reported to increase gradually year by year by Prof. Tominaga in the annual meeting of the Chemical Society of Japan. Are there any data concerning to the concentration of R-113 in the stratosphere?

3. Factors to be considered for CFC substitutes

Chlorodifluoromethane (R-22) is still one of the best alternatives to R-12, but the improvement of the refrigeration system may be necessary because of its rather high pressure. On the other hand, some CFC substitutes such as R-134a, R-124 and R-124a are expected to be able to apply to the existing system. Even so, the price of these substitutes should be less than 1,000 yen/Kg especially for the applications of mobile air conditioning.

In the case of foam blowing agents, the restriction of CFC emission by closed systems or the conversion to non-CFC systems (LPG or CO₂) have been studied intensively by users. Taking into consideration on these competitive circumstances, the price of the CFC substitutes should be limited to less than 500 yen/Kg. The solubility parameter (SP value) as well as the range of boiling points is another important factor for foam blowing agents.

In the case of solvents, conversion to aqueous systems or to hydrocarbon solvent systems have been studied by users, but the cleaning power of the aqueous systems seems to be inadequate and the hydrocarbon solvent systems are of danger because of their flammability. Therefore, the studies

should be focused on much more complete recycling systems.

When we consider some alternatives of R-113 solvent, such factors as an appropriate stabilizer and a hydrocarbon ingredient to improve its cleaning power should be considered in addition to the price range of 500 - 1,000 yen/Kg.

The problems anticipated for the full-scale production of CFC substitutes greatly depend upon the reaction systems. For example, many perfluorinated compounds such as perfluorotrialkyl amines or perfluoroethers are advantageously produced by electrochemical fluorination or direct fluorination in a relatively small-scale quantities as compared with the mass production of R-11 and R-12. Therefore it may be necessary in these reaction systems to study the possibility of the larger scale production of several hundred tons per year and to make the scale-up factor clear.

On the other hand, it is relatively easy to understand what the key factors will be in case of catalytic reaction systems. For example, R-123 and R-133a have already been studied in pilot plants and only 2-3 years will be enough for the full-scale production. As for R-134a or other substitutes with three carbons, it will take 2 years for fundamental research, and 2-3 years for pilot-scale development for the establishment of industrial procedures.

The costs of CFC substitutes will largely depend upon the performance of catalysts and the difficulties of purification..

4. Additional comments on CFC substitutes

(1) R-227a ($\text{CHF}_2\text{CF}_2\text{CF}_3$, b.p. -19.9°C) and RC-216 (perfluorocyclopropane, b.p. -31.5°C) can be added as new candidates for refrigeration purpose in place of R-12, based on their good adaptabilities to refrigeration cycles.

(2) Among the compounds listed in the Washington meeting,

R-14 and R-116 are not proper as R-12 alternatives because of too low critical temperature. R-125 will be able to use only for a limited purpose because of relatively low critical temperature (67°C).

(3) Perfluorinated compounds generally show relatively low latent heat of vaporization. Therefore, new developments of systems will be necessary for the improvement of the capacity of refrigeration.

(4) Perfluorinated compounds such as cyclic ethers and C_6F_{14} and C_7F_{16} will not be proper for solvents because of poor solubilities in hydrocarbons.

At present, several definite candidates are proposed and have been studied extensively, but we have to continue the efforts to list up more and more possible candidates.

TABLE 1. REQUIRED BOUNDARY CONDITIONS FOR FOAM BLOWING CFC SUBSTITUTES

Resin (CFC)	Boundary Conditions		CFC substitutes
	b.p. range (°C)	SP value ^{0.5} (cal/cc)	
Polystyrene (R-12)	-50 - 0	5.0 - 7.5	R-124, R-124a R-134, R-134a
Polyethylene (R-114)	-20 - 30	5.0 - 7.5	R-124, R-124a R-133a, R-134
Polyurethane (R-11)	0 - 50	6.5 - 9.0	R-123, R-123a R-123b, R-133 R-133a, R-133b R-141b, R-142
Phenol Resin (R-113)	20 - 70	6.0 - 8.0	R-123, R-123a R-123b, R-132b R-132c, R-141b

TABLE 2. PHYSICAL PROPERTIES OF R-227A AND RC-216

CFC Substitute	b.p.	Pressure of vaporization ² (kg/cm ²)	Pressure for condensation ² (kg/cm ²)	Capacity for refrigeration ³ (Kcal/m ³)	SP value ^{0.5} (cal/cc)
R-12	-29.8	3.14	15.58	415	5.97
R-22	-40.8	5.06	24.82	672	6.44
R-124	-12	1.66	10.27	245	6.42
R-124a	-10.2	1.59	9.52	230	6.24
R-134	-19.7	2.90	15.60	360	6.24
R-134a	-26.5	2.78	14.12	341	6.14
R-227a	-19.9	2.21	12.23	265	5.38
Rc-216	-31.5	2.80	10.94	290	5.22